STUDIES IN THE FLUORANTHENE SERIES.

by

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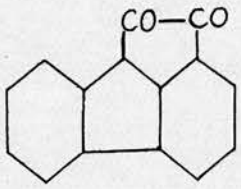
INDEX.

INTRODUCTION.

The early chemistry of fluoranthene is somewhat indefinite and obscure. Bödecker (Ann. Chem. Pharm., 1844, 52, 100) obtained a hydrocarbon from the crude mercury ores of Idria which he named Idryl. Goldschmiedt (Ber., 1877, 10, 2022) investigated this 'hydrocarbon' Idryl and found that it was a mixture of several known hydrocarbons, anthracene ($C_{14}H_{10}$), phenanthrene ($C_{14}H_{10}$), chrysene ($C_{18}H_{12}$) and pyrene ($C_{16}H_{10}$). In addition to these there was one other new hydrocarbon to which he gave the name Idryl, since it was found to have the same composition as Bödecker's crude Idryl, but different properties. Analysis and vapour density determinations showed Idryl to have the composition $C_{15}H_{10}$. Goldschmiedt described some of the physical properties of the hydrocarbon together with the formation of a bromo compound, picrate and quinone. He also described (Ber., 1878, 11, 1578) the isolation of the hydrocarbon from the mercury ores by distillation or by extraction with xylene followed by crystallisation from xylene.

About the same time Fittig and Gebhard (Ber.,1877, 10, 2141) and (Ann., 1878, 193, 142) isolated the same hydrocarbon from a high boiling fraction of coal tar. They supported Goldschmiedt's formula $C_{15}H_{10}$ and showed the formation of a trinitro compound with fuming/

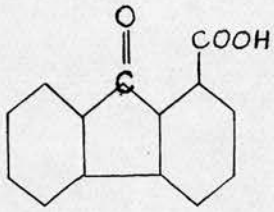
fuming nitric acid. By oxidation with chromic acid they obtained a quinone (I) and an acid $C_{14}H_8O_3$ ~~which~~ which was converted into fluorene (IV) by distillation with zinc dust and into diphenylene ketone (fluorenone) (V) when heated with soda lime. They were thus able to advance structures for the acid (II) and the hydrocarbon (III). When fluorenone-1-carboxylic acid was fused with potassium hydroxide isodiphenic acid (VI) was obtained which was oxidised with potassium dichromate and sulphuric acid to isophthalic acid (VII). In view of the relationship of the new hydrocarbon to fluorene (IV) they called it fluoranthene. This work was supported by Fittig and Liepmann (Ber., 1879, 12, 163). These authors, in a further paper (Ann., 1880, 200, 1), gave a detailed account of the oxidation products of fluoranthene which gave further support to its constitution and its relation to fluorene. The quinone (I), obtained by oxidation with chromic acid, melted at 188°C. and formed a stable complex with the parent hydrocarbon. The composition of the acid (II) was further proved by reduction with sodium amalgam into fluorenic acid (VIII) which yielded fluorene (IV) on distillation with lime.



FLUORANTHENE

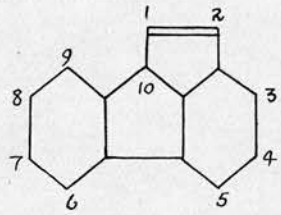
QUINONE.

I.



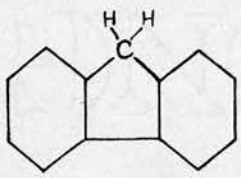
FLUORENONE-1-COOH.

II.



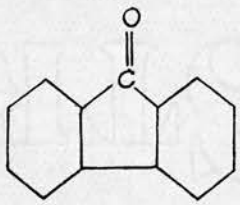
FLUORANTHENE.

III.



FLUORENE.

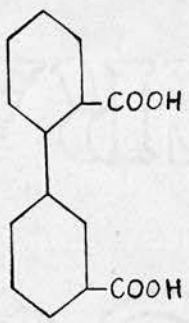
IV.



DIPHENYLENE-KETONE.

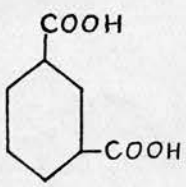
(FLUORENONE.)

V.



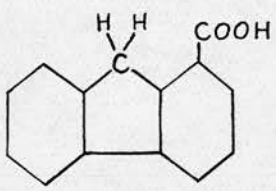
ISODIPHENIC ACID.

VI.



ISOPHTHALIC ACID.

VII.



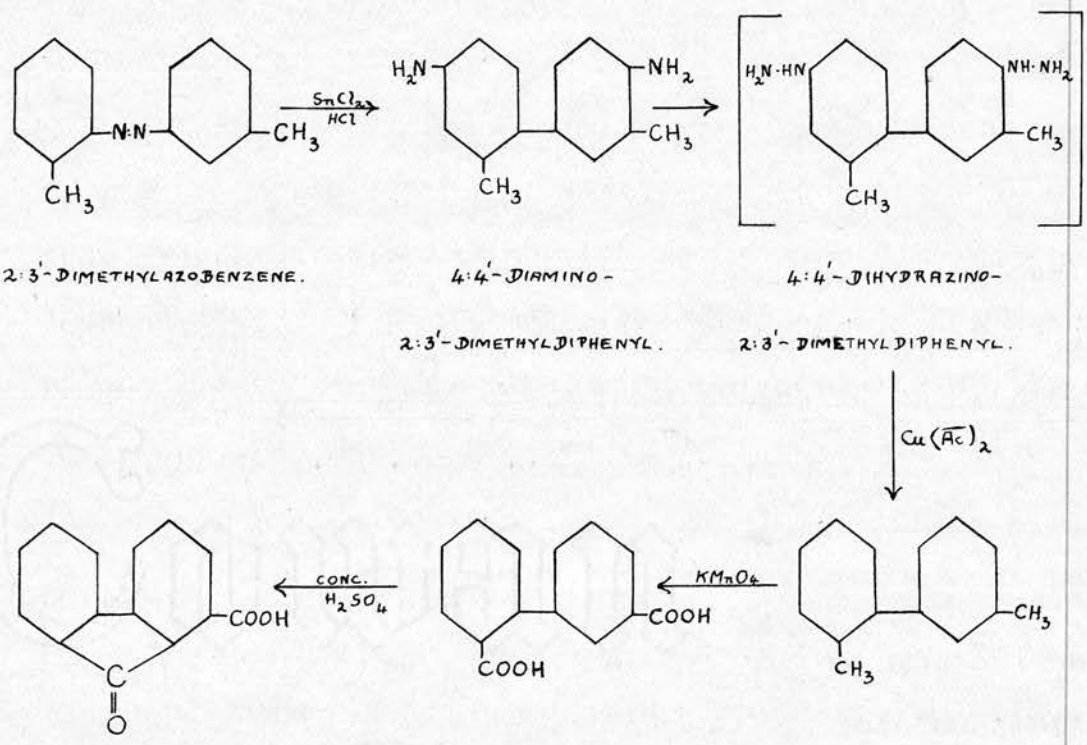
FLUORENE-1-COOH.

(FLUORENIC ACID.)

VIII.

In two further papers, (Wien. Akad. Ber. [2 Abth.] 81, 415) and (Monats. 1880, 1, 221), Goldschmiedt, still calling the hydrocarbon Idryl, reported the formation of a trichloro- and tribromo- derivative and described the reduction with phosphorus and hydriodic acid at 180°C. to give a hydrocarbon $C_{15}H_{12}$ (M.P. 76°C.) which formed a picrate. Reduction at higher temperatures, 240-250°C., gave an oily hydrocarbon $C_{15}H_{18}$. He also described the formation of a disulphonic acid by dissolving Idryl in concentrated sulphuric acid and the formation of a monocarboxylic acid by means of the nitrile. Goldschmiedt (Monats., 1902, 23, 886) prepared derivatives of fluorenone as follows:- (1) the acid chloride of fluorenone-1-carboxylic acid by the action of thionyl chloride on the acid, (2) 1-aminofluorenone by the action of bromine and potassium hydroxide on the acid amide, (3) 1-hydroxyfluorenone by diazotisation of the amine. He also described some derivatives of these compounds.

Mayer and Freitag (Ber., 1921, 54, 347) were able to synthesise diphenyl-2:3'-dicarboxylic acid (isodiphenic acid) and convert this into fluorenone-1-carboxylic acid according to the following scheme:-



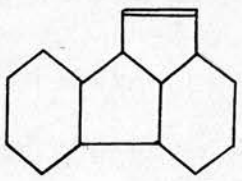
2:3'-DIMETHYLAZOBENZENE. 4:4'-DIAMINO-2:3'-DIMETHYLDIPHENYL. 4:4'-DIHYDRAZINO-2:3'-DIMETHYLDIPHENYL.

2:3'-DIMETHYLDIPHENYL. DIPHENYL-2:3'-DICARBOXYLIC (ISODIPHENIC) ACID. FLUORENONE-1-CARBOXYLIC ACID.

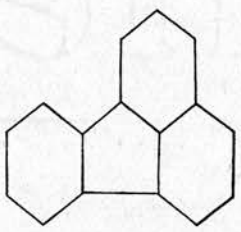
This work supplemented the earlier work of Fittig and Gebhard (loc. cit.) on the oxidation products of fluoranthene and so gave valuable confirmation to the apparent structure and formula for fluoranthene.

In 1929 von Braun and Anton (Ber., 1929, 62, 145) took up the study of fluoranthene. Since then most of the modern work on fluoranthene has been carried out/

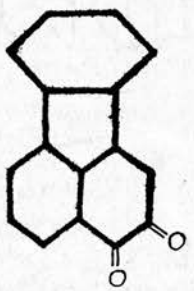
out by von Braun and his coworkers. They showed that the accepted formula for fluoranthene did not agree with the Sachse-Mohr conceptions of the stability of fused ring systems. According to the Sachse-Mohr theory a 5- and a 6-, two 6-, a 5- and a 7-, a 6- and a 7-, but not two 5- membered rings could be fused adjacently to a benzene nucleus to form a stable tricyclic compound. Thus a tetracyclic compound such as (I) below would be highly unstable, whereas a compound such as (II) would be quite stable and easily prepared.



I.



II.



III.

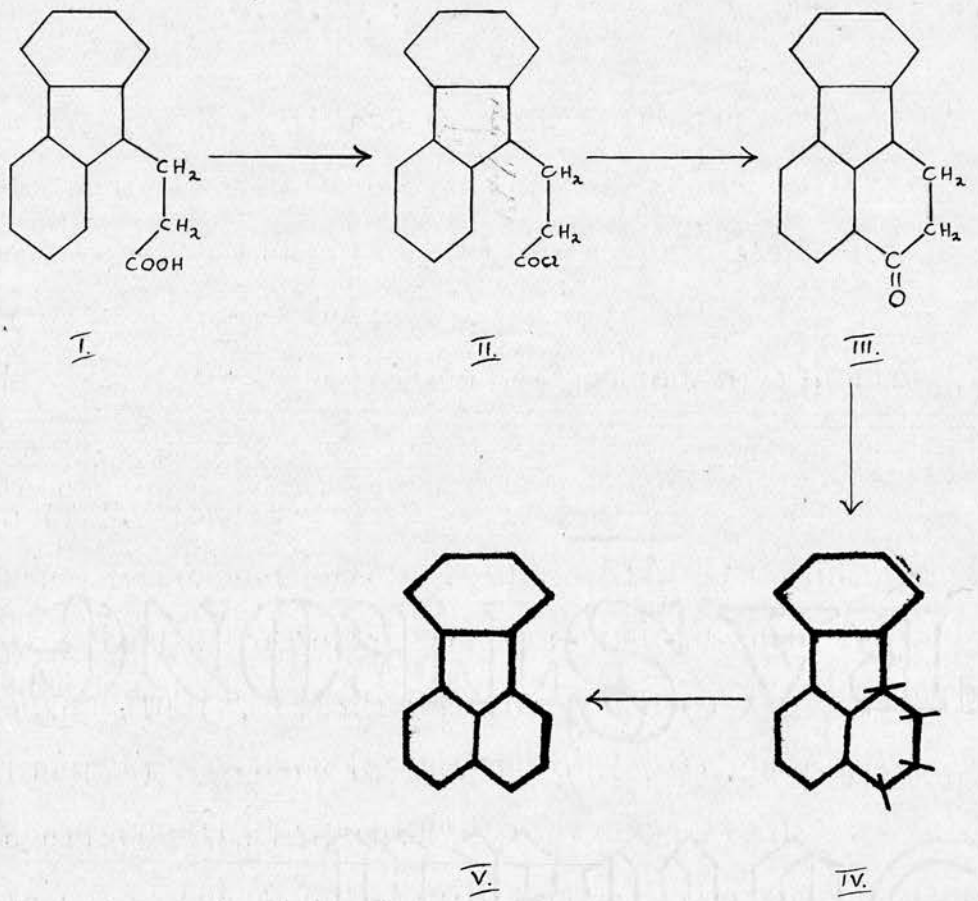
Von Braun and Anton pointed out that the analysis figures for fluoranthene and fluoranthene quinone would not be very different with the presence of one more carbon atom in each of the molecules —

C /

$C_{15}H_{10}$ requires C, 94.74%; H, 5.26%. $C_{16}H_{10}$ requires C,95.05%;H,4.95

$C_{15}H_8O_2$ requires C,81.82%; H, 3.64%. $C_{16}H_8O_2$ requires C,82.05%:H,4.27

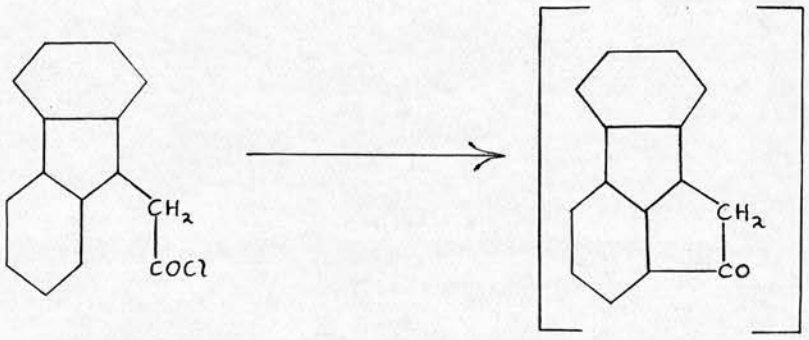
—and proposed the structure (II), which represents fluoranthene as being a derivative of naphthalene and not of indene. Fluoranthene quinone was given the corresponding structure (III). The presence of fluorenone-1-COOH as an oxidation product of fluoranthene could be explained equally well by either formula (I) or (II). They were able to prove that the formula (II) was the correct one by synthesising fluoranthene according to the following scheme:- β-9-fluorenylpropionic acid (I, below) was converted to the acid chloride (II) by means of thionyl chloride, which was then cyclised with aluminium chloride in light petroleum to give 4-keto-1:2:3:4-tetrahydrofluoranthene (III). Reduction with amalgamated zinc and hydrochloric acid (Clemmensen) gave 1:2:3:4-tetrahydrofluoranthene (IV), and this was oxidised with lead oxide to fluoranthene (V).



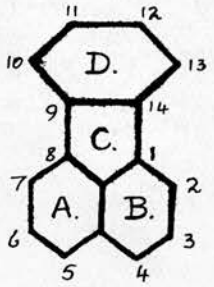
I. II. III.

IV. V.

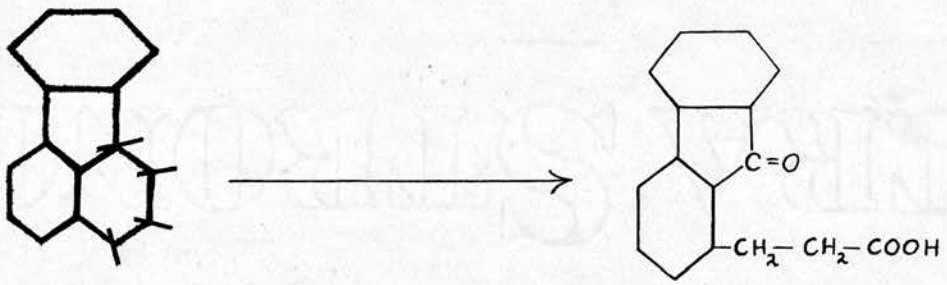
It was also shown that a comparable synthesis to support the structure of fluoranthene as an indene derivative was impossible since 9-fluorenylacetyl chloride could not be cyclised to the corresponding keto compound.



Von Braun and Manz (Ber., 1930, 63, 2608) reported their work on the hydrogenation of fluoranthene in comparison with the products obtained by Goldschmiedt (loc. cit.). With sodium amalgam at 180°C., 1:2:3:4-tetrahydrofluoranthene was obtained which did not form a picrate. On reduction with hydrogen in the presence of nickel in decahydronaphthalene, 1:2:3:4:9:10:11:12:13:14-decahydrofluoranthene was obtained. The work showed that reduction occurred progressively in rings B and D and finally in ring A to give perhydrofluoranthene.



Kruber (Ber., 1931, 64, 84) reported the isolation of 1:2:3:4-tetrahydrofluoranthene by treatment of a high boiling fraction of coal tar in solvent naphtha with sodium. Oxidation of tetrahydrofluoranthene with sodium dichromate in glacial acetic acid gave fluorenone-8-β-propionic acid.

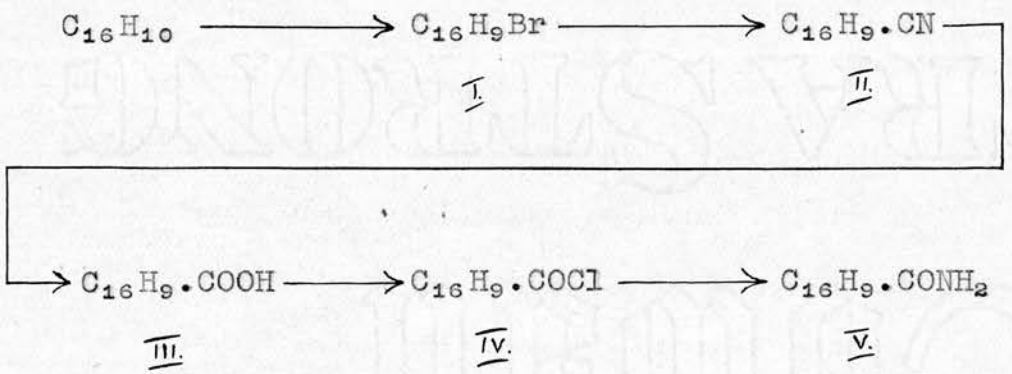


By the action of sodium and dry carbon dioxide on tetrahydrofluoranthene a monocarboxylic acid was obtained, M.P. 188°C.

Von Braun and Manz (Ann., 1931, 488, 111) gave a detailed account of their work on the monosubstitution derivatives of fluoranthene. They prepared the monobromo-, sulpho- and nitro- derivatives and showed that these three were correspondingly substituted fluoranthenes by conversion into common compounds as shown below:-

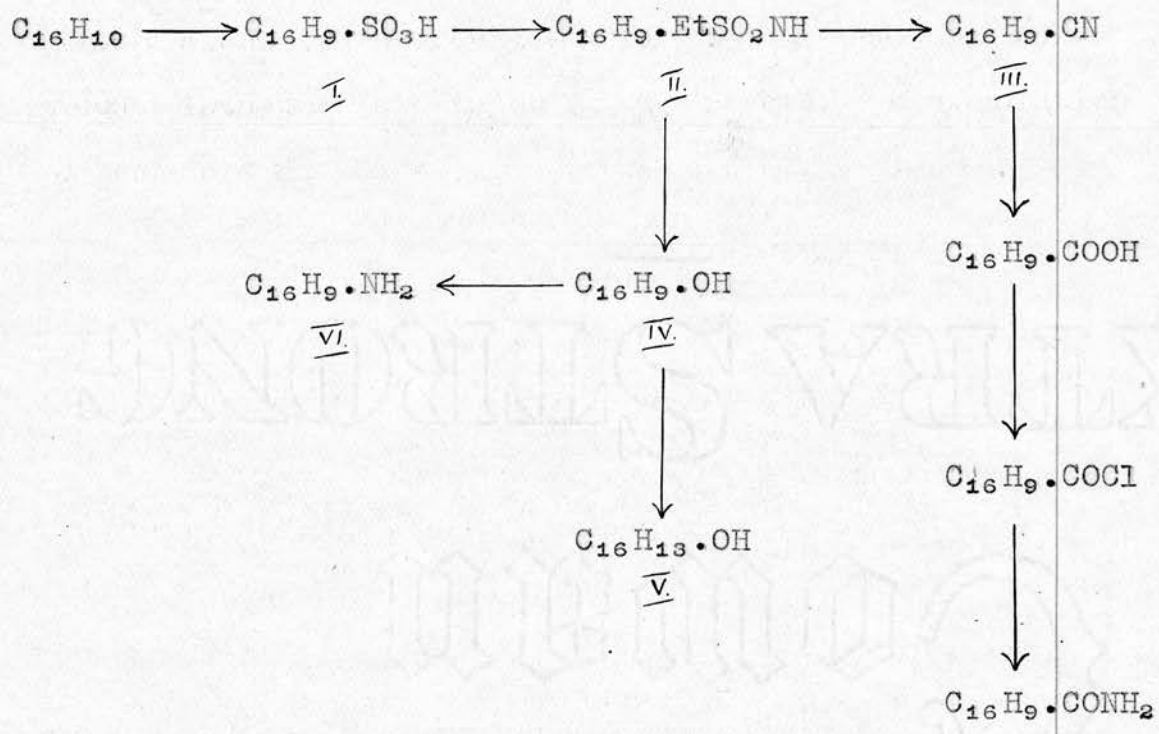
(1) /

(1) Bromination occurred when bromine was added to a boiling solution of fluoranthene in carbon disulphide. The mono-bromo- derivative (I) was separated from the mixture by means of its picrate. This bromo- derivative gave a cyano derivative (II) on treatment with potassium cyanide, which was converted into an acid (III) by hydrolysing with hydrochloric acid. The acid was converted into the acid-amide (V) by reacting on a solution of the acid chloride (IV) in benzene with ammonia.



(2) The sulphonic acid (I) was prepared by reacting on a solution of fluoranthene in chloroform with chlorsulphonic acid. On treatment with ethylamine the sulphonic acid gave the sulphoethylamide (II). By treating with a mixture of sodium and potassium cyanides this gave the same cyano derivative (III) as was obtained from the monobromo derivative above and by a corresponding series of reactions gave the same acid, acid chloride and acid amide. By reaction with caustic/

caustic potash at 340-350°C. the sulphoethylamide (II) gave a phenol (IV) which was reduced to a tetrahydrophenol (V). By reaction of the phenol (IV) with alcoholic ammonia at 300°C. an amine (VI) was obtained.



(3) The nitro derivative (I) was prepared by reacting on fluoranthene in glacial acetic acid with concentrated nitric acid. This was reduced to the corresponding amine (II) which was converted into the phenol (III) by heating with normal hydrochloric acid at 230°C. This phenol proved to be identical with that obtained from/

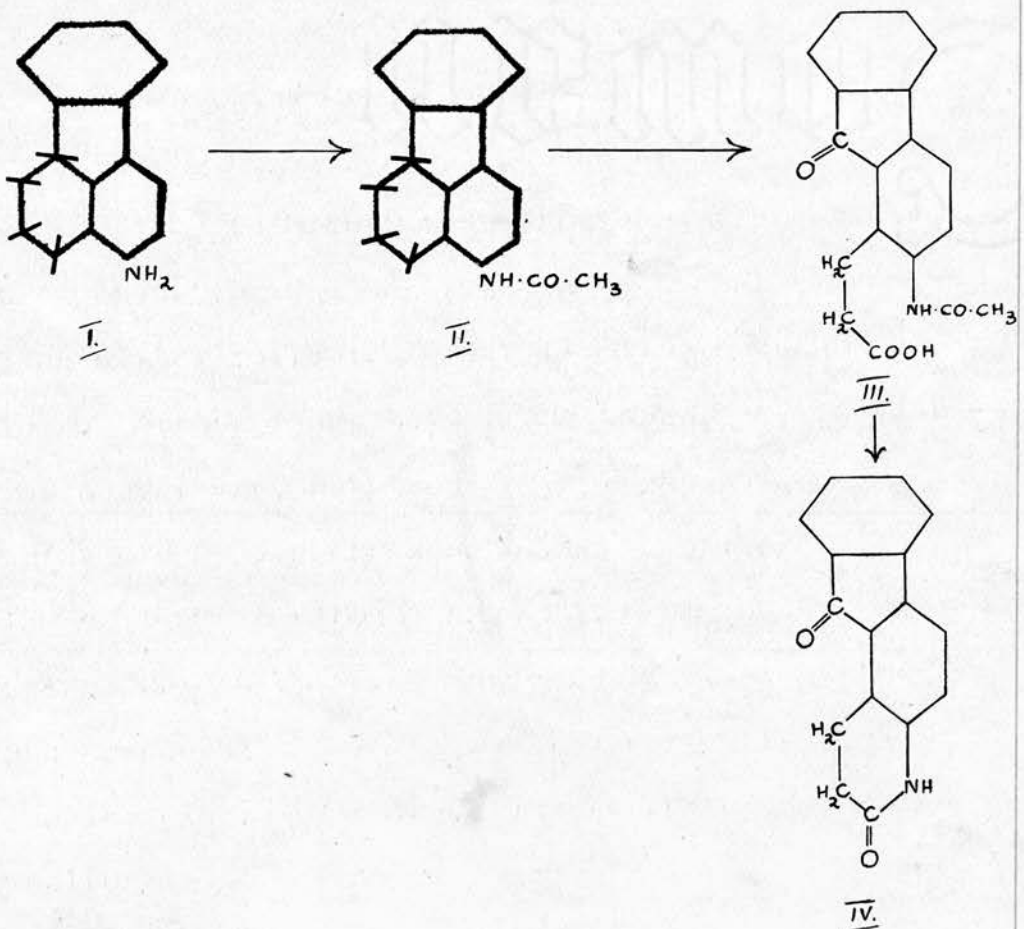
from the sulphonic acid above.

$$C_{16}H_{10} \longrightarrow C_{16}H_9.NO_2 \longrightarrow C_{16}H_9.NH_2 \longrightarrow C_{16}H_9.OH$$

I. II. III.

Von Braun and Manz set about the task of orientating these six derivatives, bromo-, sulpho-, nitro-, carboxylic acid, phenol and amine, realising that when the substituting position was fixed for one derivative then the others fell naturally into the same category. Of the five possibilities for monosubstitution 2-, 3-, 4-, 12- (11-) or 13-(10-), they proved that the derivatives which they had obtained were 4- derivatives. The fact that bromofluoranthene was easily reduced with sodium amalgam to give tetrahydrofluoranthene indicated that substitution had occurred in the naphthalene nucleus of the molecule rather than in the benzene nucleus. It was found that reduction of 4-keto-tetrahydrofluoranthene, obtained in the synthesis of fluoranthene by von Braun and Anton (loc. cit.), with sodium amalgam in alcohol gave a phenol whose phenylurethane derivative was identical with that of the tetrahydrophenol obtained from fluoranthene-monosulphonic acid (see above). The tetrahydrophenols themselves/

themselves were not identical, as proved by mixed melting-point, but they were thought to be optical isomers. The amine, obtained by reducing nitrofluoranthene, was reduced to the tetrahydroamine (I, below) and acetylated (II). This was oxidised with sodium dichromate and glacial acetic acid to a keto-carboxylic acid (III) with the same number of carbon atoms (cf. Kruber, loc. cit.). On deacetylation this passed spontaneously into a lactam (IV) with loss of water. With the amino group in any other position than the 4- this final lactamisation would not have been possible.

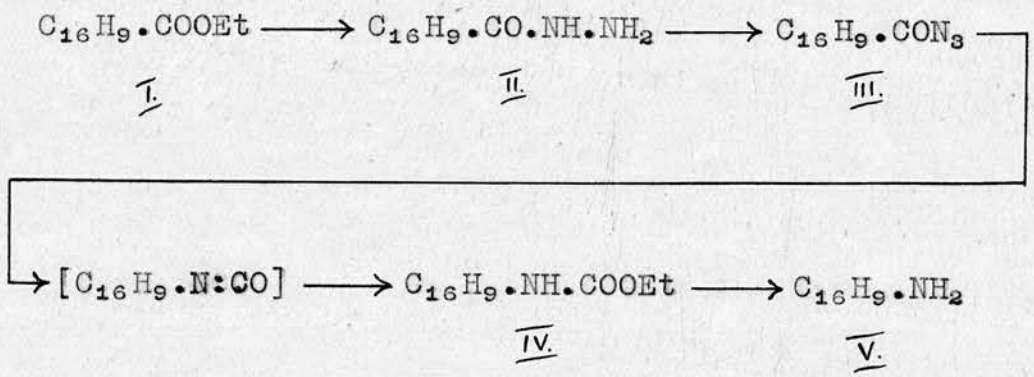


I. II. III. IV.

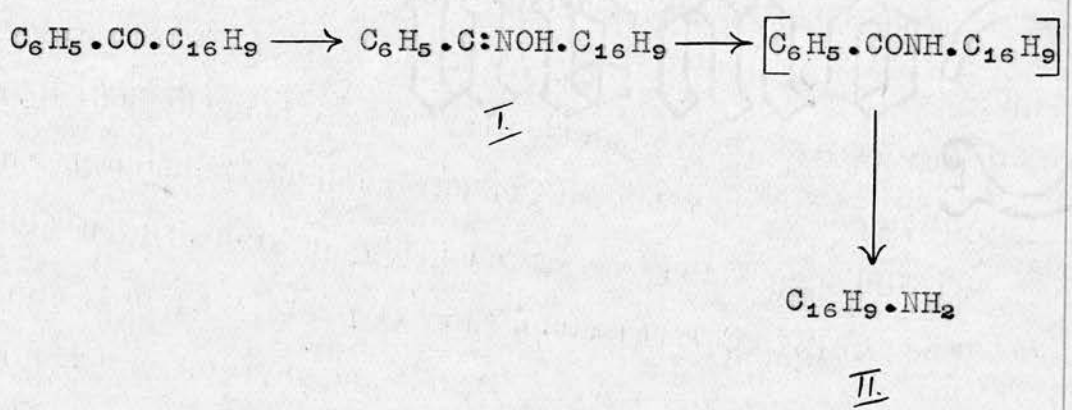
It follows, therefore, that when fluoranthene is brominated, sulphonated or nitrated substitution occurs in the 4- position.

In a further paper (Ann., 1932, 496, 170) von Braun and Manz studied the Friedel-Crafts reactions on fluoranthene. Oxalyl chloride was found to give a mixture consisting mainly of 7 parts of one monocarboxylic acid and 3 parts of a dicarboxylic acid together with a second monocarboxylic acid in very small quantity. Benzoyl chloride gave mainly one benzoyl-fluoranthene and phthalic anhydride mainly one o-carboxybenzoyl-fluoranthene, with small amounts of a second isomer of each. Again it was found that the isomers formed in these reactions were correspondingly substituted fluoranthenes. This was done as follows:-

I. The monocarboxylic acid was converted into the ethyl ester (I) which was converted to the hydrazide (II) by the action of hydrazine hydrate and then to the azide (III) by the action of nitrous acid. A Curtius rearrangement on (III) gave the urethane (IV) which was hydrolysed to the amine (V).



II. The benzoyl-fluoranthene was converted to the oxime (I) and a Beckmann rearrangement on this with benzene sulphonyl chloride and pyridine followed by hydrolysis gave an amine (II).

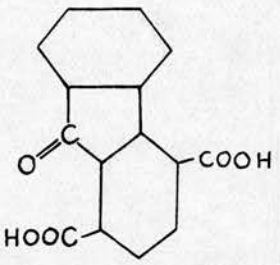


III. The o-carboxybenzoyl-fluoranthene was treated similarly to give an amine.

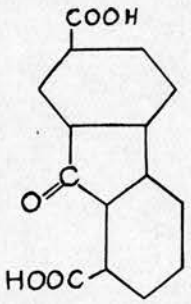
It was shown that these three amines were identical but were different from 4-amino-fluoranthene obtained by/

by reducing the nitro compound (loc. cit.). It was also shown by a similar series of reactions that the amine obtained from the isomers, produced in small quantity in the Friedel-Crafts reactions, was identical with 4-amino-fluoranthene. It seemed then, from the evidence available, that bromination, nitration and sulphonation gave mainly the 4-isomer whereas acylation gave mainly an isomer which was NOT the 4-isomer together with a very small quantity of the 4-isomer. The problem was to find out the substituting position in the fluoranthene molecule for this second series of isomers.

Von Braun and Manz attacked this problem by work on the monocarboxylic acid obtained in the Friedel-Crafts reaction. On oxidation this fluoranthene-carboxylic acid gave a mixture of fluorenone-dicarboxylic acids. They argued that if the -COOH were in the 2- or 3- position of the fluoranthene molecule then only one fluorenone dicarboxylic acid would be obtained, (I) or (II) below. The fact that two isomers were obtained fixed the substituting position to 12- (11-) or 13- (10-). In this case either ring A or B of the fluoranthene nucleus could be ruptured by oxidation giving the isomeric mixtures (III) and (IV) or (V) and (VI).



I.



III.

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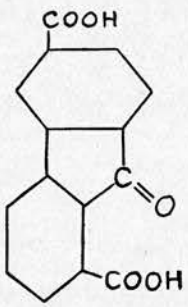
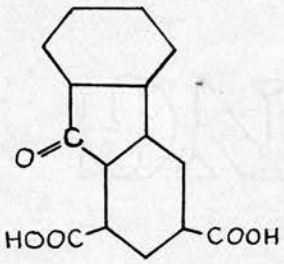


IV.



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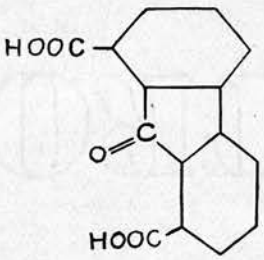

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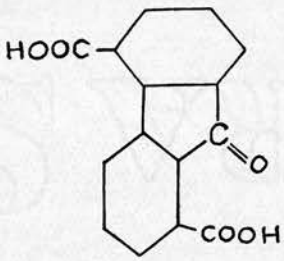
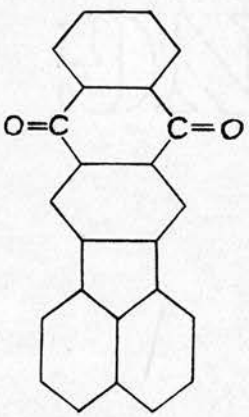
AND



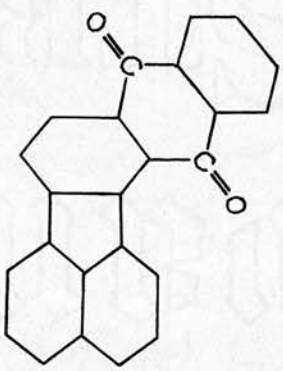
VI.

By further work on the o-carboxybenzoyl-fluoranthene they were able to show that the second substituting position was actually the 12-(11-) position. This substance was cyclised by heating in trichlorobenzene when two distinct quinones were obtained. It was pointed out that with the o-carboxybenzoyl group in the 13-(10-) position only one quinone (II) was possible whereas with the substituent in the 12-(11-) position two/

two quinones (I) and (II) were possible. When (II) was distilled with zinc dust the hydrocarbon (III) was obtained. Oxidation of (II) gave a mixture of isomeric phthaloyl-fluorenone carboxylic acids (IV) and (V) which were decarboxylated to the corresponding anthraquinone-fluorenones (VI) and (VII). Oxidation of (I) on the other hand gave a single phthaloyl-fluorenone carboxylic acid (VIII) which yielded the anthraquinone-fluorenone (IX) on decarboxylation.



I.



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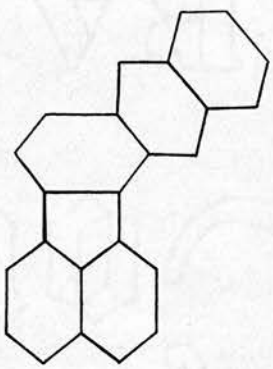
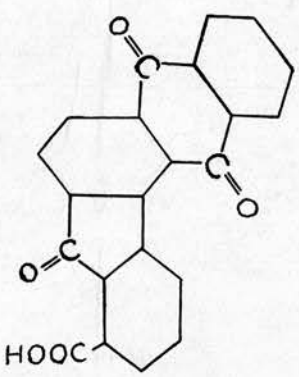


III.



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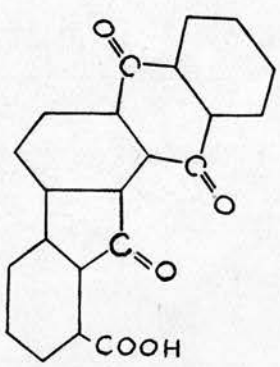

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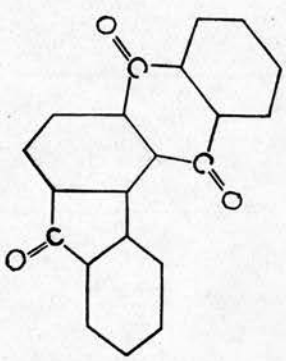

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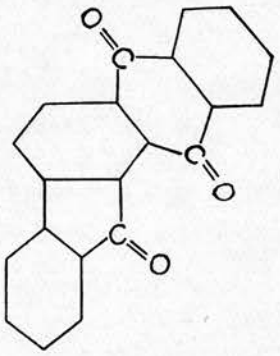

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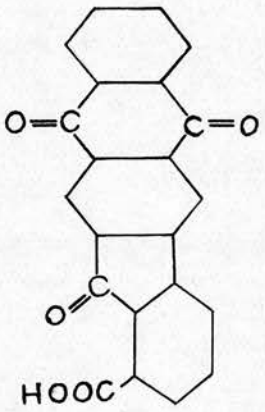

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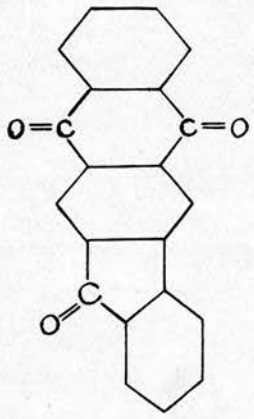
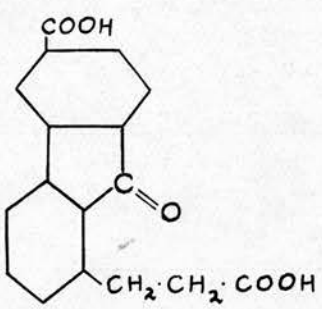
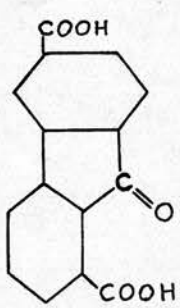


IX.

That the position of substitution was 12-(11-) was compatible with the results of further work in which the fluoranthene carboxylic acid was reduced to the 5:6:7:8-(1:2:3:4-) tetrahydrofluoranthene carboxylic acid and this was oxidised first of all to the fluorenone-6-COOH-1-β-propionic acid (I) and further to fluorenone-1:6-dicarboxylic acid.



I.



II.

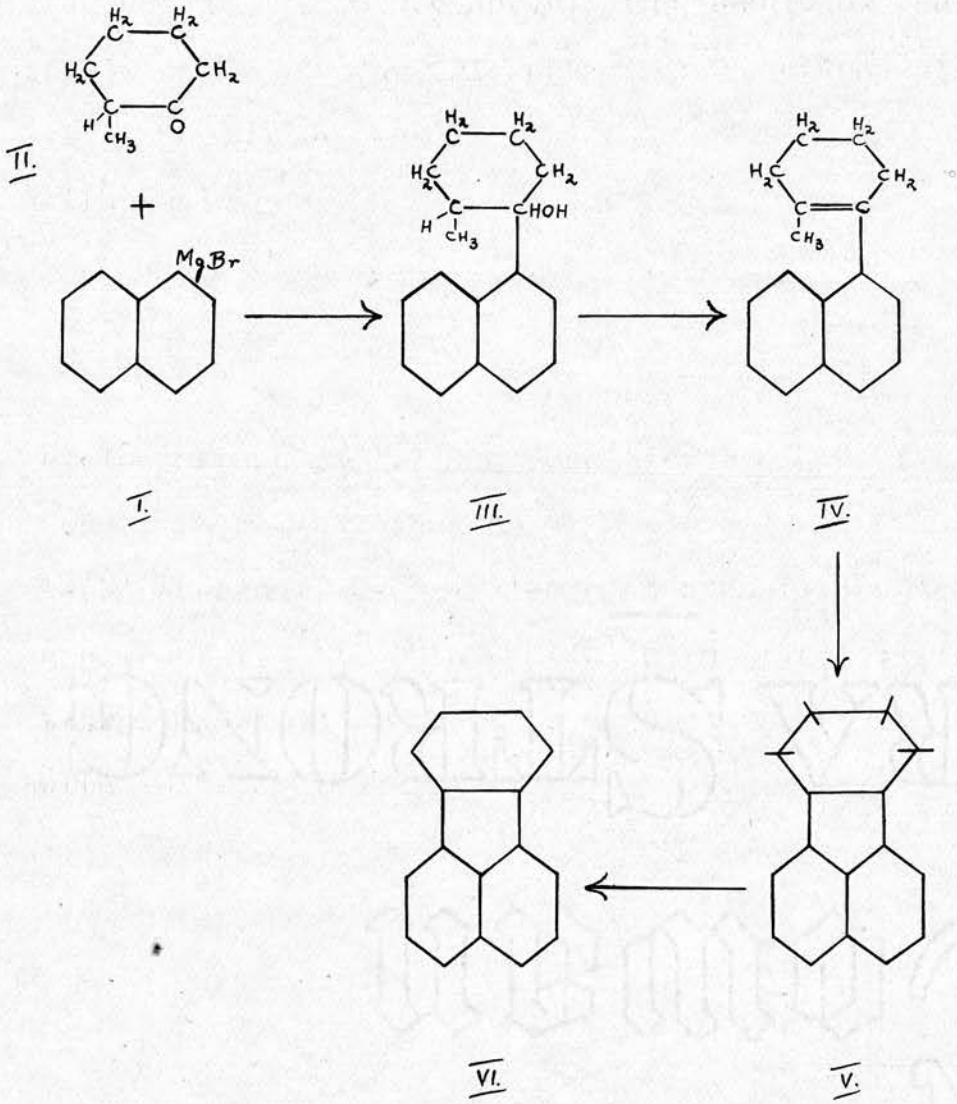
Von Braun and Manz also reported some work on the substitution of tetrahydro-fluoranthene and showed that the substituents enter exclusively the 4-position to give the 4-substituted (Br-, -SO_2Cl, phthaloyl-) 5:6:7:8-tetrahydro derivatives. It was also shown that a small amount of the 12-(11-) isomer could be isolated, in addition to the bulk of the 4-isomer when fluoranthene was brominated or nitrated. The 4-bromo- and 4-nitro- were oxidised to the corresponding 1-COOH-2-Br- and 1-COOH-2-NO_2-fluorenone. The 4-COOH-fluoranthene was oxidised to 1:2-dicarboxy-fluorenone which formed an anhydride.

Von Braun and Manz were unable to give a satisfactory explanation of the formation of the 4-derivatives as the main products in some substitution reactions and of 12- derivatives in others. To them this seemed anomalous in view of the fact that with a Friedel-Crafts reaction, phthalic anhydride gave chiefly the 12-o-carboxybenzoyl derivative with fluoranthene but only the 4-o-carboxybenzoyl derivative with 5:6:7:8-tetrahydrofluoranthene.

In a further paper von Braun and Anton (Ber., 1934, 67, 1051) studied the substitution reactions on 1-phenylnaphthalene which differs from fluoranthene only in the absence of the bond between carbon atoms 8 and 9. They found that the mono-sulphonic acid formed/

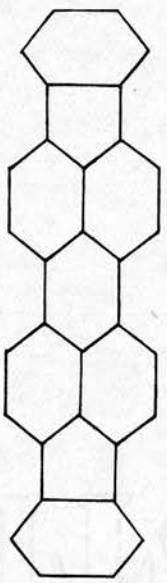
formed was almost exclusively the 4-sulpho- but they found that the Friedel-Crafts reactions also attacked the 4- position which was not in agreement with their work on fluoranthene.

Cook and Lawrence (J. Chem. Soc., 1936, 1431) achieved a synthesis of fluoranthene. 1-Naphthyl magnesium bromide (I) was condensed with 2-methyl-cyclohexanone (II). The resulting carbinol (III) was dehydrated with potassium hydrogen sulphate to give 1-(1'-naphthyl)-2-CH_3-Δ^1-cyclohexene (IV) which was cyclised with aluminium chloride to give 10:11:12:13-tetrahydrofluoranthene (V). This was dehydrogenated with selenium to give fluoranthene (VI).



Von Braun and Manz (Ber., 1937, 70, 1603), in an effort to prepare 4-amino-fluoranthene by a simpler method than reduction of 4-nitro-fluoranthene, which involves a wasteful separation from 12-nitro-fluoranthene, tried to aminate the hydrocarbon using sodamide in/

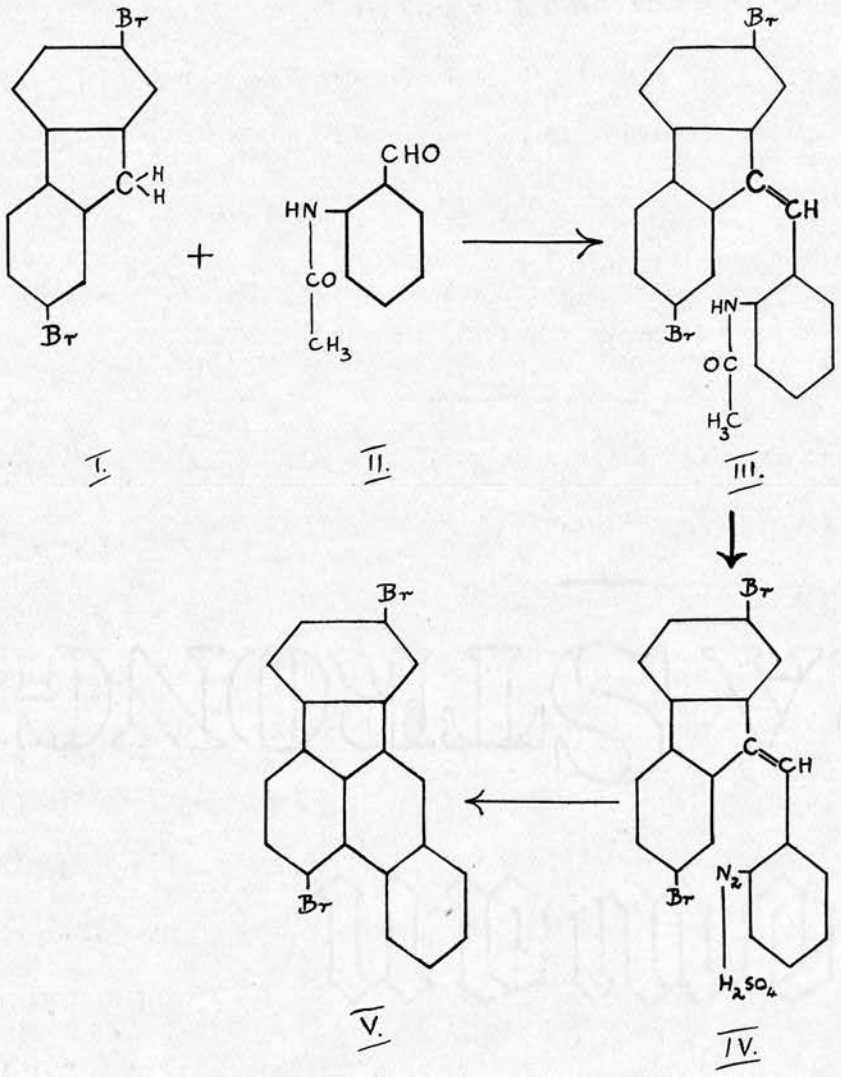
in boiling xylene and unexpectedly obtained the substance



That this structure - the only likely one - was correct was proved by the fact that 4-methyl and 4-phenyl-fluoranthene, prepared from 4-keto-tetrahydrofluoranthene by a Grignard reaction followed by dehydrogenation, did not give any of this substance. The products obtained by hydrogenation of this substance were studied fairly extensively.

Tobler, Holbro, Sutter and Kern (Helv. Chim. Acta, 1941, 24, 100E) described the preparation of 4-bromo-fluoranthene by brominating tetrahydrofluoranthene and dehydrogenating with chloranil in boiling xylene. In this way the troublesome isolation of 4-bromo-fluoranthene from a mixture of isomers was overcome. The preparations/

preparations of dibromofluoranthene and dibromotetrahydrofluoranthene were also described. It was thought, by analogy with fluoranthene disulphonic acid, that this dibromofluoranthene should be the 4:11- compound. The disulphonic acid obtained by sulphonating fluoranthene gave a dihydroxy compound by alkali fusion which was easily oxidised to a substance which probably is a quinone. With the substituents in the 4:12- positions a quinone grouping would be impossible. An attempt to synthesise 4:11-dibromo-fluoranthene from 2:7-dibromo-fluorene by following the synthesis of von Braun and Manz was unsuccessful. A successful synthesis of 4:11-dibromo-5:6-benzofluoranthene was accomplished. 2:7-Dibromofluorene (I) was condensed with 2-acetylamino-benzaldehyde (II) in the presence of sodium ethoxide to give 2:7-dibromo-9-(2-acetylaminobenzylidene)-fluorene (III). This was hydrolysed to the free amine and diazotised with amyl nitrite in sulphuric acid.(IV) was cyclised to (V) by heating. This was reduced with sodium amalgam to octahydro-5:6-benzofluoranthene which was dehydrogenated to 5:6-benzofluoranthene. The preparation of a tri-Br- and tetra-Br-fluoranthene was also described.

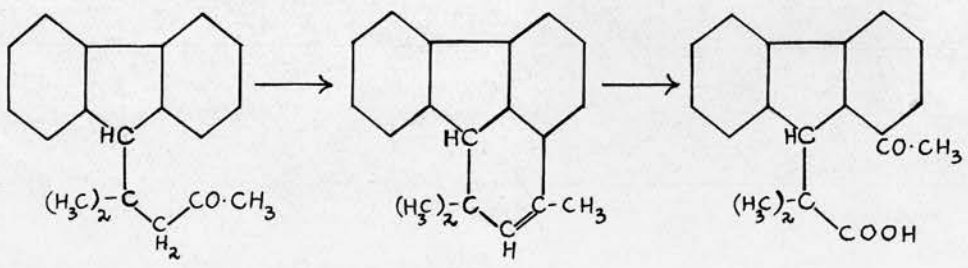


I. II. III. IV. V.

Buu-Hoï and Cagniant (Rec. Trav. Chim., 1943, 62, 719) in dealing with 2-substituted quinolines derived from fluoranthene described the preparation of 12-(11-) acetyl-fluoranthene by a Friedel-Crafts reaction. The semicarbazone and oxime were prepared and the oxime transformed by Beckmann rearrangement into 12-acetyl-amino-fluoranthene which was claimed to be identical with that which von Braun and Manz obtained by direct acetylation of 12-amino-fluoranthene. Buu-Hoï and Cagniant/

Cagniant were unable to separate a second monoacetyl isomer or a diacetyl compound, thus confirming von Braun's belief that acylation proceeded primarily in the 12-position.

France, Tucker and Forrest (J. Chem. Soc., 1945,7) synthesised 2:2:4-trimethyl-1:2-dihydrofluoranthene (II) by condensing fluorene and acetone in presence of caustic potash to give methyl-2(9-fluorenyl)-2-methyl-propyl ketone (I) which gave (II) on treatment with hydrobromic acid in glacial acetic acid for 1 hour. (II) was catalytically reduced with palladium black in alcohol to give 2:2:4-trimethyl-1:2:3:4-tetrahydro-fluoranthene. The structure of (II) was proved by partial oxidation with acetone and potassium permanganate to 1-acetylfluorene-9-α-isobutyric acid (III) which yielded a mixture of 1-acetyl-9-fluorenone and fluorenone-1-carboxylic acid on further oxidation with sodium dichromate.



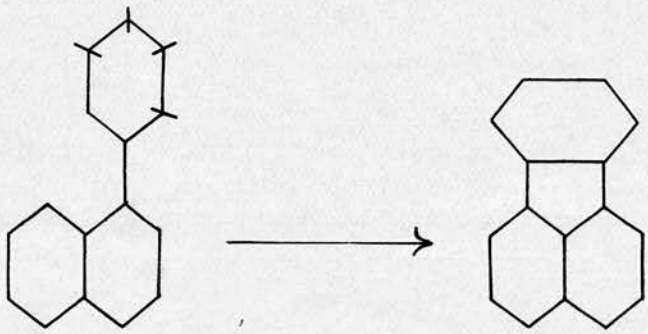
I. II. III.

Orchin and Woolfolk (J.A.C.S., 1946, 68, 1727) reported the preparation of a sharp melting 2:4:7-trinitrofluorene molecular complex with (amongst other polynuclear compounds) fluoranthene. These complexes are claimed to be superior to the picrates because of their enhanced insolubility in organic solvents.

Moureu, Chovin and Rivoal (Compt. Rend., 1946, 223, 951) prepared synthetically the new hydrocarbon 2:3:1':8'-binaphthylene (11:12-benzofluoranthene).

Hoffmann and Tagmann (Helv. Chim. Acta, 1947, 30, 288) described the preparation of compounds of 1:2:3:4-tetrahydrofluoranthene and 2:2:4-trimethyl-1:2:3:4-tetrahydrofluoranthene, containing activated groups of the type $-CH_2.CH_2.N(CH_3)_2$ in the 1-position, for tests in pharmacology.

Orchin and Reggel (J.A.C.S., 1947, 69, 505) synthesised fluoranthene by a cyclodehydration of 1-(2:3:4:5-tetrahydrophenyl)-naphthalene (I), prepared from naphthyl magnesium bromide and cyclohexanone, over palladium charcoal or a mixture of chromic anhydride and alumina, the latter giving a better yield of fluoranthene.



I.

Since 1932, the patent literature has contained some thirty-five patents covering compounds of fluoranthene and their potential uses in the dyestuffs industry. These compounds include the mono- and di-bromo-, cyano-, carboxylic acids, sulphonic acids and related hydroxy bodies as well as a few polyfunctional compounds.

OBJECT OF RESEARCH.

It seemed desirable to repeat some of the work already covered by von Braun with a view to clarifying, if possible, the position whereby bromination, nitration and sulphonation were found to give chiefly the 4-isomer whereas acylation gave chiefly the 12-(11-) isomer. It was hoped that the mixtures obtained in acylation would be more thoroughly separated into their component isomers by the use of chromatographic methods than they had been by the wasteful methods of fractional crystallisation - the only methods available to von Braun and his coworkers before the renaissance of chromatography. In this way it was hoped to obtain a clearer picture of acylation in the fluoranthene nucleus. It was also foreseen that opportunities might arise of confirming the orientation of these acylated-fluoranthenes. Such opportunities have been taken wherever possible.

EXPERIMENTAL SECTION - INTRODUCTION.

The experimental work which was done in the course of this research is described in the following pages. Melting-points of substances were determined by two methods: (1) on a micro-melting-point apparatus (Kofler, Mikrochem., 1934, 15, 242) which gave a very good indication of purity as judged by sharpness of melting point; (2) by capillary-tube method (Campbell, 'Qualitative Organic Chemistry', p. 7, fig. 4). The first method was largely used in the course of the work to estimate the purity of fractions obtained by chromatographic analyses. All substances which were analysed, all mixed melting-points and all key compounds were checked by both methods.

Compounds were analysed by Drs. Weiler and Strauss of Oxford, using micro-analytical methods.

Yields of products are given as percentages of the maximum theoretical amounts obtainable.

Chromatographic analyses were followed, wherever possible, by means of the distinctive fluorescent bands which were visible when the columns were viewed under the ultra-violet lamp.

EXPERIMENTAL

Benzoylation of Fluoranthene by the Perrier Modification of the Friedel-Crafts Reaction.

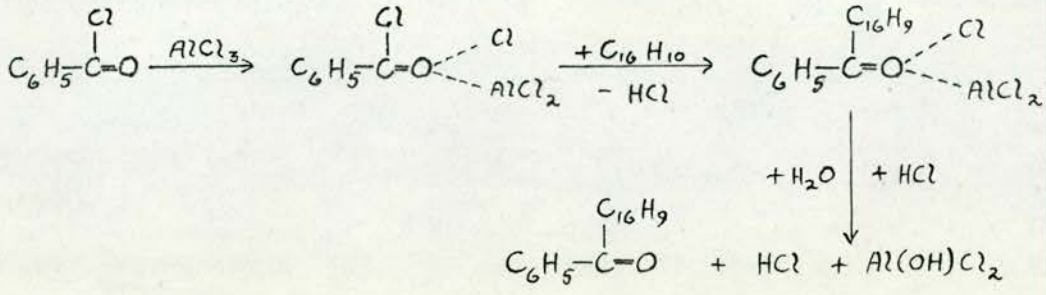
cf. Fieser's 'Experiments in Organic Chemistry', p. 192.

Freshly powdered aluminium chloride (17.5 g.) was slowly added to benzoyl chloride (17.5 g.) with shaking. The mass was heated gently and allowed to cool. Carbon disulphide (100 c.c.) was added and as much as possible of the solid taken into solution by heating on the steam-bath. The solution was allowed to cool slightly. Fluoranthene (25 g.) was added over half an hour resulting in a brisk evolution of HCl fumes. The slurry was maintained at steam-bath temperature with stirring for 10 minutes and was then cooled thoroughly in ice. The resultant solid complex was separated by filtration.

The solid obtained was stirred into water (375 c.c.) and conc. hydrochloric acid (25 c.c.), and boiled for 15 minutes to ensure complete decomposition. The dark brown oil turned semi-solid on cooling in ice. This 'solid' was extracted with ether (1 litre), the ethereal layer washed with Na_2CO_3 solution and finally with water and dried over anhydrous calcium chloride. The bulk of the ether was distilled off. Yellow crystals separated on standing.

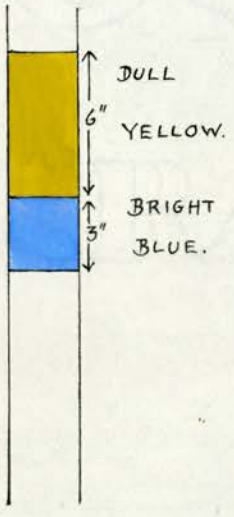
Yield. 25 g. ≡ 66% theoretical.

Equation for Reaction.



BENZOYL- FLUORANTHENE.

The crude solid (5 g.) was dissolved in cold benzene (60 c.c.) and chromatographed on a column of alumina (24" long x 0.86" diameter). The solid was adsorbed as a visible yellow band but under the ultra-violet lamp the column appeared as shown in the accompanying diagram with a bright blue fluorescent band emerging from the dull yellow band. On development with (1) benzene (50 c.c.) followed by (2) 2:1 mixture of benzene and light petroleum (60-80°) the band system broadened and moved down the column but the bands did not separate. Development was continued with the benzene/light petroleum mixture and fractions were eluted as shown below. Each fraction was worked up by distilling off the bulk of the solvent and leaving the residual volume - in each case/



case 20-25 c.c. - to deposit crystals.

A. Bright blue fluorescent band.

This crystallised to give 0.28 g. of white crystals which fluoresced blue under the ultra-violet lamp. M.P. 105-108° C.

B. A cut between the blue fluorescent and visible yellow bands.

This gave 0.40 g. bright yellow crystals, yielding small yellow prisms after two crystallisations from light petroleum (60-80°). M.P. 127.5-129.5° C. with sintering.

C. Visible yellow band.

This gave 2.80 g. yellow solid which was crystallised from a 4:1 mixture of light petroleum (80-100°) and benzene. Two crystal forms separated, a white and a yellow form. An attempt was made to 'hand-pick' a crystal of each form and determine the M.P., but nothing conclusive was obtained from this.

Yellow crystal	-	M.P. 92-102°C.
White crystal	-	87-126°C.
Random sample	-	90-115°C.

D. After-runnings of visible yellow band.

This gave 0.89 g. yellow solid which had a M.P. 91-117°C. after crystallisation from a 4:1 mixture of light petroleum (80-100°) and benzene.

Recovery from the column = 4.37 g. ≡ 87.4% Th.

Conclusion /

Conclusion: The column gave a partial separation of the crude mixture into (a) a white material which fluoresces blue, (b) a yellow material, and (c) a third substance believed to be colourless.

An attempt was made to crystallise the crude solid (1 g.) M.P. 78-105° C., from a 4:1 mixture of light petroleum (80-100°) and benzene. A yellow solid (0.10 g.) separated on standing overnight, M.P. 124.5-130°C. The filtrate was evaporated to dryness giving a deep yellow coloured oil which would not solidify. This oil was crystallised from light petroleum (80-100°) and yielded a mixture of white and yellow crystals. The white crystals, M.P. 84-116°C., fluoresced blue under the ultra-violet lamp.

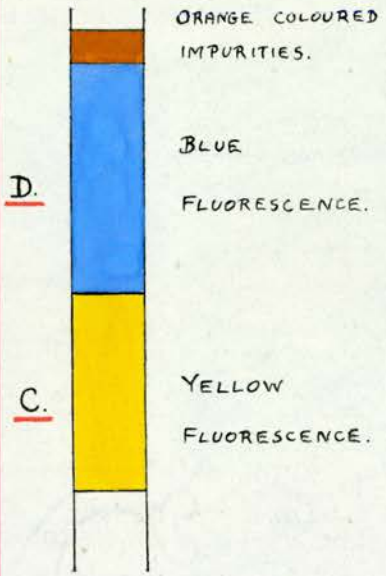
A further attempt was made to purify the crude solid by a combination of the two methods already tried.

The crude solid (5 g.) was crystallised from a 4:1 mixture of light petroleum (80-100°) and benzene. A yellow solid separated which on crystallisation from light petroleum (80-100°) had a M.P. 89-110°C.

The mother liquor of the yellow solid was chromatographed on a column of alumina (28" long x 0.86" diameter). When adsorption was complete the appearance of the chromatogram was similar to that shown in the diagram on p. 33 , but the yellow band

was/

was less intense. The column was developed with the same light petroleum/benzene mixture when the blue fluorescent band separated from the yellow band and was eluted. Development was continued until the column appeared as shown in the accompanying diagram. The column was drained, extruded and cut into sections as shown. Each section was extracted with several portions of boiling alcohol. Finally the solvent was distilled from each fraction and the residual volume left to deposit crystals.



A. Blue-fluorescent material eluted from the column.

This gave colourless needle-shaped crystals which fluoresced blue under the ultra-violet lamp. M.P. 108-110°C. Mixed M.P. with fluoranthene gave no depression.

B. Continued mixed solvent elution.

Nothing was obtained from this fraction.

C. Yellow fluorescent band.

This gave yellow solid M.P. 124-128°C., which was crystallised from alcohol plus a little glacial acetic acid yielding yellow needles, M.P.129-131.5°C.

D./

D. Top blue fluorescent band.

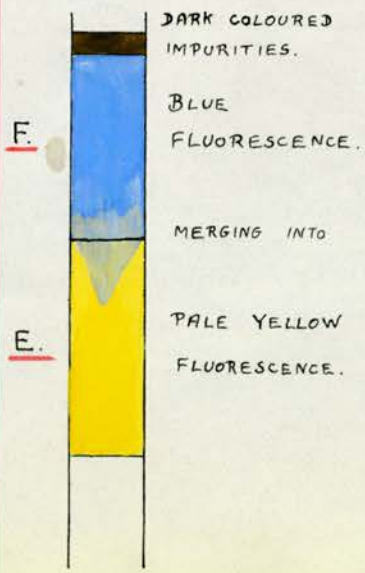
This gave first of all a crop of yellow crystals (D_1) which proved to be identical with the material from fraction C. M.P. 122-127°C.

A white solid (D_2) next separated in the supernatant alcohol. This was immediately decanted and left to crystallise separately. M.P. 118-121.5°C. with sintering.

A mixed M.P. with the crystals obtained in fractions C and D_2 was 86-112°C.

This column was not carried through on a quantitative basis but showed the possibility of separating the crude mixture into three pure components.

The crude solid (5 g.) was dissolved in a 4:1 mixture of light petroleum (80-100°) and benzene and chromatographed on a column of alumina (28" long x 0.86" diameter). When adsorption was complete, the appearance of the chromatogram was identical with that shown in the diagram on p.33 . Development was carried out with the mixed solvent. Fractions were collected as shown below. The blue fluorescent material was completely eluted and this was followed by the almost complete elution of the dull yellow fluorescent material. The column was then drained and appeared as shown/



shown in the accompanying diagram. The alumina was extruded and cut into sections which were extracted with alcohol. The separate fractions were worked up in the usual way.

A. Blue fluorescent material eluted from the column.

This gave 0.46 g. white crystals which fluoresced blue under the ultra-violet lamp, M.P. 109-110°C. Mixed M.P. with fluoranthene gave no depression.

B. Dull greenish-yellow fluorescent material eluted from the column.

This gave 1.10 g. yellow solid M.P. 116-127°C. which was crystallised from alcohol. Yellow elongated prisms M.P. 129-130°C. This substance was analysed for benzoyl-fluoranthene as follows:-

$C_{23}H_{14}O$ requires C, 90.2%; H, 4.6%.

found C, 90.22%; H, 4.65%.

C. A further fraction of yellow coloured eluate.

This gave 1.08 g. yellow solid M.P. 119-128°C.

D. The drainings of the column.

This gave 0.24 g. pale yellow solid M.P. 88-105°C. which was crystallised from alcohol M.P. 94-108°C.

E. Bottom part of column extracted with alcohol.

This gave 1.42 g. solid which was mostly white but had a little yellow material admixed.

F. Blue fluorescent part of column extracted with alcohol.

This gave 0.61 g. white solid which on

crystallisation/

crystallisation from alcohol gave white hexagonal plates which fluoresced blue under the ultra-violet lamp. M.P. 120-121°C.

A mixed M.P. with a sample of fluoranthene gave 81-108°C.

This substance was analysed for benzoyl-fluoranthene as follows:-

$C_{23}H_{14}O$ requires C, 90.2%; H, 4.6%.

found C, 89.74%; H, 4.6%.

Recovery from the column = 4.91 g ≡ 98% Th.

Fractions D (crystallised) and E of this chromatogram were rechromatographed in an attempt to obtain an absolute separation of the isomers. The mixed solid (1.61 g.) was dissolved in a 4:1 mixture of light petroleum(80-100°) and benzene and chromatographed on a column of alumina (17" long x 0.86" diameter). On development with the same light petroleum/benzene mixture the column assumed a similar appearance to that shown in the diagram on p.37 . The yellow band was eluted as a separate fraction followed by a cut between the yellow and blue fluorescent bands. Finally the column was eluted with alcohol. The fractions were worked up in the usual way.

A. Yellow fluorescent band.

This gave 0.35 g. of a mixture of yellow and white/

white crystals. M.P. 95-115°C.

B. Cut between yellow and blue fluorescent bands.

This gave 0.19 g. almost white solid M.P. 100-115°C.

C. Alcoholic eluate.

This gave 0.51 g. white crystals M.P. 118.5-121°C. The column still showed a distinct blue fluorescence under the ultra-violet lamp.

Conclusion: Although an absolute separation of the two benzoyl-fluoranthene isomers was not achieved, the figures for the last two chromatographic analyses gave a strong indication that the two isomers were present in approximately equal amounts in the original mixture.

An unsuccessful attempt was made to separate the two isomers by fractional crystallisation of the picrates. The picrate was prepared from the crude mixture (2 g.) as detailed in Campbell's "Organic Qualitative Analysis", p. 84. The resultant picrate was crystallised from gradually increased volumes of boiling alcohol and spot melting-points were taken on each crop of crystals. Whatever volume of alcohol was used it was not found possible to obtain a sharp-melting picrate.

The final picrate, M.P. 122-139°C., was decomposed with ammonia and the benzoyl-fluoranthene extracted/

extracted with methylene chloride. The solid was crystallised from alcohol, M.P. 87-105°C.

An attempt was made to separate the benzoyl-fluoranthene isomers by fractional crystallisation of their oximes.

The mixed oxime of the crude benzoyl-fluoranthene (5.6 g.) was prepared as detailed on p. 51. The crude oxime was dissolved in alcohol and allowed to crystallise.

Fraction A Oxime. M.P. 206-215°C. Recrystallised from alcohol M.P. 218-226°C.

The alcoholic mother liquor from the crude oxime was reduced to half volume and a further crop of crystals obtained.

Fraction B Oxime. M.P. 165-188°C.

The mother liquor from fraction B crystals was evaporated to dryness yielding an oil which turned to solid on trituration with alcohol.

Fraction C Oxime. M.P. 182-212°C.

Partial separation of the isomers by means of their oximes was thus possible. (cf. melting-points of the oximes of the pure isomers on pp.51 and 52).

Benzoylation/

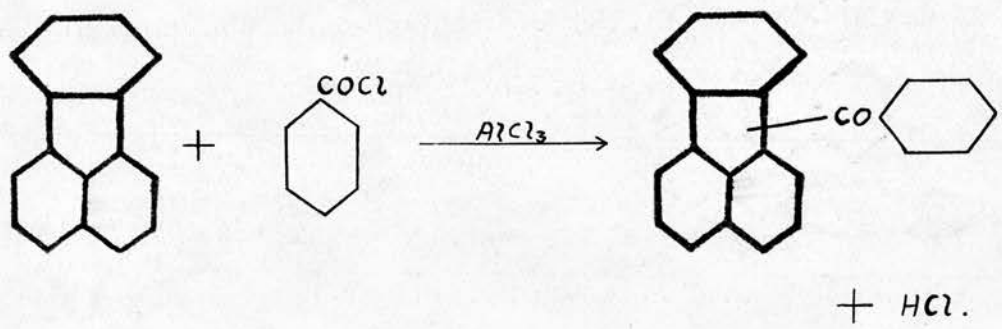
Benzoylation of Fluoranthene.

von Braun and Manz. Annalen. 1932, 496, 184.

Fluoranthene (25 g.) and powdered aluminium chloride (17.5 g.) were agitated in carbon disulphide (150 c.c.) with ice-cooling. Benzoyl chloride (17.5 g.) was added dropwise and the whole agitated for 8 hours. at room temperature. The reaction mixture was heated on the water bath for 6 hours and the carbon disulphide then removed by distillation. The brown mass which remained was decomposed with ice giving a yellow oily solid. This solid was extracted with ether, washed with sodium carbonate solution and then with water and finally dried over anhydrous calcium chloride. The ether was distilled off giving a dark yellow semi-solid mass.

Yield = 31 g. crude solid ≡ 81.9% Th.

Equation for Reaction



An attempt was made to purify this solid by chromatography. The crude solid (31 g.) was dissolved in the minimum volume of cold benzene and chromatographed on a column of alumina (20" long x 1.38" diameter). The solid was adsorbed as a broad yellow band, 8" long, which had a dull fluorescence in daylight. On development with benzene the yellow band broadened until the column appeared uniformly yellow but no separation could be detected. Four fractions, each of 120 c.c. of benzene eluate, were collected followed by two fractions, each of 100 c.c. of 5% alcohol in benzene. The column was then quite clear. Each fraction was worked up in the usual way and yielded an impure oily mixture which could not be made to crystallise even on prolonged trituration.

It was obvious that this attempt at purification had been unsuccessful. All the fractions from this chromatographic analysis were therefore combined again.

The picrate of the crude solid was prepared from boiling alcoholic solutions. The crude picrate, M.P. 106-139°C., was crystallised from a mixture of alcohol plus 10% glacial acetic acid. M.P. of crystallised material, 116-145°C.

This crystallised picrate was decomposed with concentrated/

concentrated ammonia, the resultant benzoyl-fluoranthene extracted with methylene chloride, washed with water until free from ammonia and dried over anhydrous calcium chloride. The solvent was removed by distillation leaving an orange coloured oil which changed to a yellow solid on trituration with alcohol.

This crude benzoyl-fluoranthene (15 g.), M.P. 85-102°C., was dissolved in benzene and chromatographed on a column of alumina (20" long x 1.38" diameter). The solid was adsorbed as a yellow band at the top of the column. The column was developed with benzene when a blue-fluorescent material emerged from the yellow band. An attempt was made to follow the development under the ultra-violet lamp and so elute the several fractions but 'coning' developed in the column (see accompanying diagram) so that the blue fluorescent material became contaminated with the yellow material. When the yellow band was completely eluted the column was drained, the alumina extruded and extracted with alcohol. The fractions were worked up in the usual way.

A. Blue-fluorescent material plus a little yellow material.

This gave 0.27 g. white needle crystals, M.P. 93-105°C.

B./

B. Main yellow fluorescent band.

This gave 12.71 g. dark yellow solid which was crystallised from a mixture of alcohol and ether.

1st crop of crystals (mainly white) M.P. 108-122°C.
2nd crop of crystals (white) M.P. 87-102°C.

C. Alcoholic extract.

This gave 0.70 g. oily residue. Nothing further was done with this.

Recovery from column = 13.68 g. = 91.2% Th.

The material obtained from fraction B of the last column was obviously still a mixture. The two crops of crystals were again mixed.

An attempt to effect partial crystallisation from light petroleum (80-100°) was not successful.

It was decided to attempt a chromatographic separation adhering as closely as possible to the conditions detailed on pp.37-38 when a successful separation of the mixture from the Perrier modification of the Friedel-Crafts reaction was obtained.

Accordingly, the crude solid from fraction B of the last chromatographic analysis (5 g.) was dissolved in a 4:1 mixture of light petroleum (80-100°) and benzene, and chromatographed on a column of alumina (25.5" long x 0.86" diameter). The solid was adsorbed as a yellow band and developed with the same light petroleum/benzene mixture. The course of the chromatogram/

chromatogram was found to follow closely that of the corresponding column described on p. 37. Fractions were collected as shown below and worked up in the usual way.

A. Blue-fluorescent material eluted from the column.

This gave 0.32 g. white solid which fluoresced blue under the ultra-violet lamp and was proved by M.P. and mixed M.P. to be fluoranthene.

B. First fraction of yellow fluorescent material eluted from the column.

This gave 0.20 g. yellow crystals M.P. 128-129.5°C.

C. A further fraction of yellow coloured eluate.

This gave 0.95 g. solid M.P. 108-123°C. which was crystallised from alcohol plus a little ether. M.P. 128.5-129.5°C.

A mixed M.P. with the corresponding material obtained from the Perrier modification of the Friedel-Crafts reaction gave no depression.

A mixed M.P. with 4-benzoyl-fluoranthene (p. 65) gave no depression proving that the yellow needle isomer is indeed the 4-substituted fluoranthene.

D. The drainings of the column.

This gave 0.97 g. yellow solid, M.P. 92-105°C. On crystallisation from alcohol plus a little ether this gave yellow crystals, M.P. 110-122°C.

The/

The oxime of this material was prepared (p.51) and crystallised from benzene, M.P. 217-222°C. A mixed M.P. with the oxime of the known high M.P. isomer benzoyl-fluoranthene (p.51) gave no depression, showing that the material of this fraction is essentially the high M.P. isomer benzoyl-fluoranthene.

E. Bottom part of column extracted with alcohol.

This gave 0.70 g. pale yellow solid, M.P.80-103°C. An unsuccessful attempt was made to purify this fraction by partially dissolving the solid in light petroleum (80-100°) and decanting the solution from the residual yellow oil. The solution deposited a white solid which was crystallised from alcohol. M.P. 95-103°C.

F. Blue fluorescent part of column.

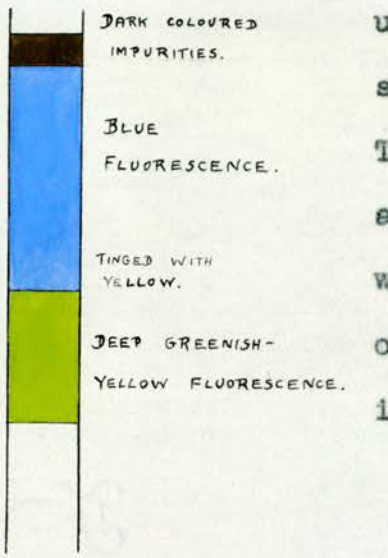
This gave 1.33 g. pale yellow solid, M.P. 85-101°C. No attempt was made to purify this by crystallisation.

Recovery from the column = 4.47 g. ≡ 89.4% Th.

Conclusion: This chromatographic analysis gave a fairly good separation of the mixture.

Fractions D, E and F of the last chromatogram (2.83 g. solid) were dissolved in benzene and chromatographed on a column of alumina (28" long x 0.86" diameter). The solid was adsorbed as a pale yellow band/ .

band and developed with a 4:1 mixture of light petroleum (80-100°) and benzene. Development was very slow so 5 drops alcohol per 100 c.c. mixed solvent were added and development continued with this mixture until the column appeared as shown in the accompanying diagram. The column was drained, extruded and cut as shown. Each fraction was extracted with several lots of boiling alcohol and worked up in the usual way.



A. Deep greenish-yellow fluorescent band.

This gave an impure solid; a mixture of white and yellow crystals.

B. Blue fluorescent band.

The first alcoholic extraction gave 0.14 g. white crystalline material, M.P. 117-120°C. which was crystallised from alcohol, M.P. 120-121°C. Further alcoholic extractions gave a mixture of white and yellow crystals.

Conclusion: This chromatographic analysis gave only slight separation of the two isomers.

The mixture of crystals obtained from fractions

A /

A and B of this last column (2.47 g.) were dissolved in benzene and rechromatographed on a column of alumina (19" long x 0.86" diameter). The column was developed with a 4:1 mixture of light petroleum (80-100°) and benzene plus 10 drops alcohol per 100 c.c. mixed solvent. The yellow fluorescent band moved down the column and was eluted leaving the blue fluorescent material on the column. Two fractions of yellow eluate were collected after which the column appeared uniformly blue under the ultra-violet lamp. The column was then drained, the alumina extruded and extracted with several lots of boiling alcohol. The fractions were worked up in the usual way.

A. First fraction of yellow fluorescent material eluted from the column.

This gave 0.37 g. yellow solid which was crystallised from alcohol. M.P. 129-130°C.

B. Cut between the yellow and blue fluorescent materials.

This gave 0.29 g. solid which crystallised from alcohol as a mixture of white and yellow crystals.

C. Blue fluorescent material extracted from the column with alcohol.

This gave 1.62 g. white solid M.P. 106-117°C. which was crystallised from alcohol giving colourless plates which fluoresced blue under the ultra-violet lamp/

lamp. M.P. 119-120°C.

A mixed M.P. with the corresponding material obtained from the Perrier modification of the Friedel-Crafts reaction gave no depression.

A mixed M.P. with 4-benzoyl-fluoranthene (p.65) gave a definite depression showing that the low M.P. isomer is probably the 11-substituted benzoyl-fluoranthene.

Recovery from the column = 2.28 g. ≡ 92.3% Th.

Conclusion: Separation as the picrate, decomposition and repeated chromatographic analysis showed the presence of two isomeric benzoyl-fluoranthenes in approximately equal amounts in the crude mixture.

Derivatives of 4-Benzoyl-Fluoranthene.

2:4-Dinitrophenylhydrazone.

This was prepared by Brady's method (Campbell, p. 87) and required nine and a half hours refluxing. This gave an orange solid, M.P. 220-240°C. with slow decomposition, which was crystallised from glacial acetic acid giving orange crystals, M.P. 260-265°C. with slight decomposition. Under the microscope the material looked clean and homogeneous.

Analysis: $C_{29}H_{18}O_4N_4$ requires N, 11.53%.
found N, 11.7%.

Picrate/

Picrate.

This was prepared according to the method given in Campbell, p. 84. The picrate formed easily in alcoholic solution. M.P. 158-160°C. with slight decomposition.

Analysis: $C_{29}H_{17}O_8N_3$ requires N, 8.42%.
found N, 8.00%.

Oxime.

4-Benzoyl-fluoranthene (0.5 g.) was refluxed with hydroxylamine hydrochloride (2 g.) in pyridine (10 c.c.) for 3 hours. Trituration with (1) water and (2) alcohol gave a greyish solid which was crystallised from iso-propyl alcohol and deposited plates on addition of a little water. M.P. 219-223°C.

Analysis: $C_{23}H_{15}ON$ requires N, 4.36%.
found N, 3.95%.

Beckmann Rearrangement on the oxime of 4-benzoyl-fluoranthene.

A mixture of the oxime (0.25 g.) and phosphorus pentachloride (0.5 g.) in anhydrous ether (45 c.c.) was left with occasional shaking for 20 hours. The ether was distilled off and the resultant yellow oil triturated with water to give a solid which was crystallised from a mixture of glacial acetic acid and alcohol. M.P. 260-263°C. This substance was analysed for the Beckmann rearrangement product (an anilide/

anilide) as follows:-

$C_{23}H_{15}ON$ requires N, 4.36%.

found N, 4.51%.

Derivatives of 11-Benzoyl Fluoranthene.

These were prepared in each case as detailed above for the corresponding derivatives of the 4-isomer.

2:4-Dinitrophenylhydrazone.

The derivative in this case formed easily and separated immediately giving a red solid M.P. 281-284° C. with decomposition.

Analysis: $C_{29}H_{18}O_4N_4$ requires N, 11.53%.

found N, 11.6%.

Picrate.

This formed easily from alcoholic solution. M.P. 128-130°C.

Analysis: $C_{29}H_{17}O_8N_3$ requires N, 8.42%.

found N, 10.2%.

Oxime.

The crude solid was crystallised from alcohol. M.P. 193-198°C. A mixed M.P. with the oxime of 4-benzoyl-fluoranthene was 175-208°C.

Analysis: $C_{23}H_{15}ON$ requires N, 4.36%.

found N, 4.22%.

Beckmann/

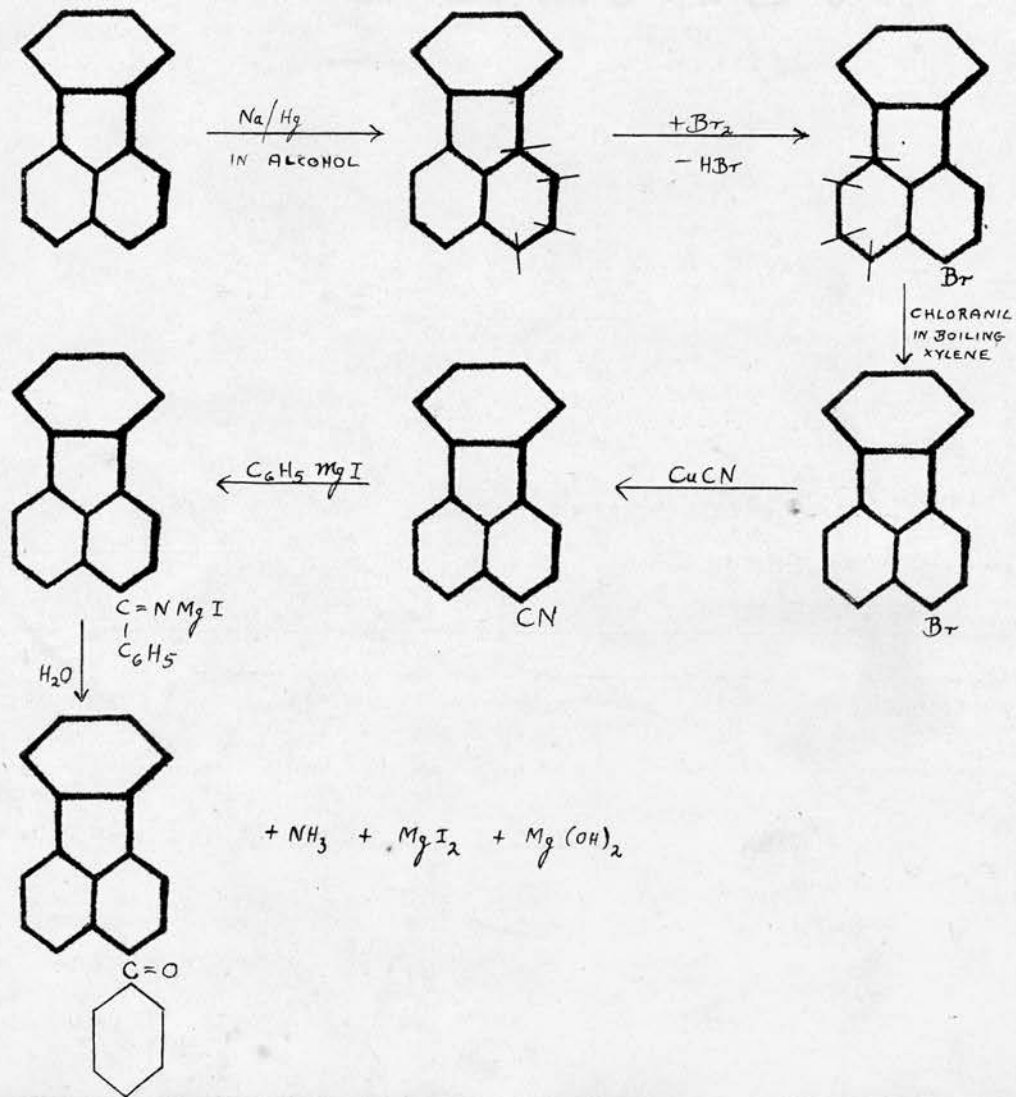
Beckmann rearrangement on oxime of 11-benzoyl-fluoranthene.

The crude solid was crystallised from alcohol, M.P. 209-214°C. A mixed M.P. with the parent oxime was 167-179°C. This substance was analysed for the Beckmann rearrangement product (an anilide) as follows:

$C_{23}H_{15}ON$ requires N, 4.36%.

found N, 4.58%.

Scheme for Synthesis of 4-Benzoyl-fluoranthene.



Preparation of 1:2:3:4-tetrahydro-fluoranthene.

von Braun and Manz. Berichte, 1930, 63, 2612.

5% Sodium amalgam was prepared according to the directions given in Fieser's 'Experiments in Organic Chemistry', p. 329.

Fluoranthene (20 g.) was dissolved in alcohol (750 c.c.) with gentle warming and 5% sodium amalgam (280 g.) added in small pieces. A brisk reaction occurred. The mixture was refluxed gently for 2 hours. Concentrated hydrochloric acid was added until the solution was neutral to litmus and the alcoholic solution diluted into 4 litres cold water, with agitation. A dirty white solid separated, M.P. 74.5-77°C. The crude solid was crystallised from alcohol, carbon screened, and was deposited as white needles, M.P. 76-77°C. A little of this material was re-crystallised from alcohol and gave long white prisms, M.P. 77-78°C.

Analysis: Calc. for $C_{16}H_{14}$ C, 93.2%; H, 6.8%.

found C, 93.19%; H, 6.53%.

Yield = 17 g. crystals = 81.5% Th.

An unsuccessful attempt was made to prepare the picrate of tetrahydrofluoranthene. This could not be formed either from alcoholic or glacial acetic acid solutions of the reactants. Unchanged tetrahydro-fluoranthene/

fluoranthene was recovered in each case.

Preparation of 4-bromo-5:6:7:8-tetrahydro-fluoranthene.

von Braun and Manz. Annalen, 1932, 496, 192.

1:2:3:4-Tetrahydro-fluoranthene (17 g.) was dissolved in glacial acetic acid (153 g.) with gentle warming. To this was added dropwise a solution of bromine (13.2 g.) in glacial acetic acid (26 g.). A precipitate formed almost as soon as the addition was complete. This was left overnight to separate completely and filtered off. The crude solid was washed on the filter with a little glacial acetic acid and then crystallised from glacial acetic acid (very soluble, hot) giving colourless plates, M.P. 131-133°C. Yield = 19 g. = 80.8% Th.

Analysis: Calc. for $C_{16}H_{13}Br$. Br, 28.04%.

found Br, 28.44%.

Attempt to prepare 4-cyano-tetrahydro-fluoranthene

cf. Organic Syntheses, vol. 21, p. 89.

4-Bromo-5:6:7:8-tetrahydro-fluoranthene (4.0 g.) was mixed with cuprous cyanide (1.53 g.) and refluxed with pure dry pyridine (10 c.c.) for 15 hours at 215-225°C. The resultant liquor was cooled to 100°C. and drowned into water (5 c.c.) plus concentrated ammonia (5 c.c.). The slurry was extracted with methylene chloride and gave a dark red-brown oil. An attempt

was/

was made to purify this by dissolving in alcohol and carbon screening but the product still came down as an oil so the alcohol was completely evaporated.

The oil was dissolved in benzene and chromatographed on a column of alumina (18" long x 0.86" diameter). The substance was adsorbed as a dark orange band. The column was developed with a 3:1 mixture of benzene and light petroleum when a visible yellow band developed and a pale yellow fluorescent material emerged from it, until the column appeared pale yellow throughout its length under the ultra-violet lamp. Development with benzene eluted the pale yellow material and caused the visible yellow band to move slowly down the column. The visible yellow band was eluted with 5% alcohol in benzene. The column showed a tendency towards 'coning' (see p. 44). Fractions were collected as shown below and worked up in the usual way.

A. Benzene/light petroleum eluate of pale yellow fluorescent material.

This gave a pale yellow solid (0.71 g.) which was crystallised from alcohol giving an almost white solid, M.P. 95-103°C. This substance was recrystallised from glacial acetic acid, M.P. 108-114°C. A mixed M.P. with 4-bromo-tetrahydrofluoranthene (M.P. /

(M.P. 131-133°C.) was 122-130°C., indicating that this fraction was impure 4-bromo-tetrahydrofluoranthene.

B. Forerunnings of visible yellow band eluted with 5% alcohol in benzene until the eluate was yellow coloured even though the column was still colourless.

This gave a yellow oil (0.26 g.) which was triturated with alcohol to a yellow solid. This was crystallised from alcohol, M.P. very indefinite, 190-230°C.

C. Further fraction of alcoholic benzene eluate collected until the column was uniformly yellow.

This gave a yellow oil (0.72 g.) which was triturated with alcohol. The solid was crystallised from alcohol giving a dark yellow solid, M.P. very indefinite, 140-190°C.

D. The main visible yellow band.

This gave a dark yellow oil (1.05 g.) which was treated as for fraction C, M.P. 170-190°C.

E. The drainings of the column.

This gave a dark red oily scum of negligible weight which was not investigated further.

Recovery = 2.74 g. ≡ 68.5% Th. from starting material.

Conclusion: This column gave a partial separation of the crude reaction mixture into slightly impure 4-bromo-tetrahydrofluoranthene and an impure solid of very/

very indefinite M.P.

The crystallised solids from fractions B, C and D were combined and recrystallised from glacial acetic acid. Water was added to bring down a dirty yellow solid, M.P. 170-190°C. with sintering.

The mother liquors from fractions B, C and D were combined and the volume reduced to about a quarter of the original. No further solid was deposited. On adding water a dirty orange oily solid was deposited. It was obvious that this was very impure and the material was not investigated further.

Dehydrogenation of 4-bromo-5:6:7:8-tetrahydro-fluoranthene.

R. Tobler and co-workers. Helv.Chim. Acta, 1941,24,104E.

4-Bromo-5:6:7:8-tetrahydro-fluoranthene (10 g.) and chloranil (17.3 g.) were refluxed together in sulphur free xylene (178 c.c.) for 24 hours. The mixture was left to cool and deposited crystals of tetrachlor-hydroquinone which was filtered and washed with a little purified xylene. The xylene filtrate (192 c.c.) was diluted with an equal volume of ether and the mixture extracted (1) with 5% caustic soda solution (70 c.c.) and (2) dilute caustic soda solution (70 c.c.). The solvent layer was thoroughly washed/

washed with water and dried over anhydrous calcium chloride. The bulk of the xylene/ether solvent was distilled off and the residual volume left to crystallise. The crude crystalline product, M.P. 102-109°C., was crystallised from light petroleum (100-120°) giving 3.02 g. crystals, M.P. 106.5-108°C. A little of this material was crystallised from alcohol giving almost colourless needles, M.P. 108-110°C. and analysed for 4-bromo-fluoranthene as follows:-

Calc. for $C_{16}H_9Br$. Br, 28.44%.

found Br, 27.94%.

The xylene mother liquor was further evaporated and gave a second crop of crude solid, M.P. 94-105°C. This was twice crystallised from light petroleum (100-120°) giving 2.52 g. material, M.P. 106-110°C. A mixed M.P. with pure 4-bromo-fluoranthene, M.P. 108-110°C., gave no depression.

Yield = 5.54 g. ≡ 55.8% Th.

During several trials it was found that a cleaner work-up of the completed dehydrogenation was obtained if no excess of chloranil was used. This confirms the experience of B.M. Barclay (Thesis, Edinburgh, 1944) when working with many carbazole compounds. (cf. Tobler and co-workers, who used a 10% excess of chloranil). It was also found to be advantageous to dilute/

dilute the xylene with an equal volume of ether before extracting with alkali. (B.M. Barclay's Thesis).

Sulphur-free xylene was prepared according to the method given in Fieser's "Experiments in Organic Chemistry", p. 313.

Attempted preparation of 4-cyano-fluoranthene.

Cf. Organic Syntheses, Vol. 21, p. 89.

4-Bromo-fluoranthene (3 g.) was mixed with cuprous cyanide (1.17 g.) and refluxed with pure dry pyridine (20 c.c.) for 16 hours. The resultant black liquor was cooled to 100°C. and drowned into water (5 c.c.) plus concentrated ammonia (5 c.c.) when a brown solid was precipitated. The slurry was extracted with a mixture of benzene (20 c.c.) and ether (40 c.c.) and separated by filtration from the solid remaining The green aqueous layer was separated and the solvent layer washed successively with (1) dilute ammonia (4 x 10 c.c.), (2) dilute hydrochloric acid (2 x 10 c.c.), (3) water (2 x 10 c.c.) and (4) saturated brine (2 x 10 c.c.). The solvent was distilled off leaving a brown solid (2.57 g.), M.P. 102-108°C. A mixed M.P. with 4-bromo-fluoranthene, M.P. 108-110°C., gave no depression (105-110°C), indicating that the desired reaction had not taken place.

Preparation/

Preparation of 4-cyano-fluoranthene.

von Braun and Manz. Annalen, 1931, 488, 116.

4-Bromo-fluoranthene (5.48 g.) was thoroughly mixed with cuprous cyanide (1.92 g.). One fifth of this mixture was used in a trial attempt.

The mixture was heated in an open tube for 6 hours at 260°C. The mass was allowed to cool and extracted twice with methylene chloride. The solvent was evaporated off giving an orange 'oily' solid, M.P. 104-112°C. A mixed M.P. with 4-bromo-fluoranthene, M.P. 108-110°C. was 97-108°C., showing by the depression that some reaction had taken place. The crude solid was crystallised from alcohol and carbon screened, M.P. 115-119°C. A mixed M.P. with 4-bromo-fluoranthene was now 99-111°C. An elements test showed the presence of nitrogen and the absence of bromine, confirming that the reaction had taken place.

The 4-cyano-fluoranthene was further crystallised from light petroleum (60-80°). 1st. crop of crystals M.P. 117-119°C.; 2nd. crop of crystals by partial evaporation of the mother liquor, M.P. 115-119°C.

This latter material (0.10 g.) was dissolved in benzene and chromatographed on a column of alumina (13" long x 0.86" diameter). The solid was adsorbed as a pale yellow band at the top of the column. On development/

development with a 2:1 mixture of light petroleum (80-100°) and benzene a blue fluorescent material emerged from the yellow band and was eluted. The yellow band, showing a greenish yellow fluorescence under the ultra-violet lamp, was collected separately. The fractions were worked up in the usual way.

A. Blue fluorescent material.

This gave an oily scum and was neglected.

B. Greenish-yellow fluorescent material.

This gave a yellow solid which was crystallised from light petroleum (80-100°), M.P. 116-121°C. This was further crystallised from alcohol but the M.P. did not improve. M.P. 117-121°C. This material was analysed for 4-cyano-fluoranthene as follows:-

Calc. for $C_{17}H_9N$. N, 6.17%.

found N, 5.58%.

The bulk of the 4-bromo-fluoranthene/cuprous cyanide mixture was heated in an open tube for 6 hours at 260°C. There was some sublimation during the early part of the heating, depositing a yellow solid This was crystallised from light petroleum (60-80°) and gave fine yellow needles, M.P. 109-112°C. A mixed M.P. with 4-bromo-fluoranthene (M.P. 108-110°C.) was 102-110°C. It was assumed that this sublimate was impure 4-cyano-fluoranthene.

The/

The bulk of the solid remaining in the tube was pulverized and extracted with methylene chloride giving an orange slightly 'oily' solid. This was crystallised from alcohol and carbon screened. M.P. 111-116°C. A mixed M.P. with 4-bromo-fluoranthene was 98-110°C. This material was not crystallised further but was used as such in the subsequent Grignard reaction.

Yield of crystallised material = 0.79 g. ≡ 18.0% Th.

Preparation of 1-benzoyl-naphthalene from 1-napthonitrile.

cf. Fieser's "Experiments in Organic Chemistry",p.67.

Acree. Ber., 1904, 37, 628.

The Grignard reagent was prepared from magnesium turnings (1.0 g.), bromobenzene (4.45 c.c.) and anhydrous ether (18.5 c.c.) as described in Fieser's book. A solution of 1-naphthonitrile (5.75 g.) in anhydrous ether (7.5 c.c.) was added dropwise and the reaction mixture refluxed for half an hour. The mixture was decomposed with 10% sulphuric acid (25 c.c.) and crushed ice (15 g.) and steam-distilled to remove any unchanged bromobenzene and other steam-volatile products. The residue was extracted with ether, the ether layer washed with dilute sulphuric acid, then with water and finally dried over anhydrous calcium chloride. The ether was distilled off leaving a dark reddish/

reddish oil which crystallised after standing 15 hours. The crude solid was pressed on porous tile and crystallised from light petroleum (60-80°). White crystals, M.P. 74-76°C. A mixed M.P. with a sample of pure 1-benzoylnaphthalene, prepared by the Friedel-Crafts reaction, gave no depression.

Attempt to prepare 4-benzoyl-fluoranthene from 4-cyano fluoranthene.

The Grignard reagent was prepared from magnesium turnings (0.10 g.), bromobenzene (0.45 c.c.) and anhydrous ether (1.85 c.c.). Assuming a 90% yield of phenyl magnesium bromide, 4-cyano-fluoranthene (0.79 g.) in boiling anhydrous ether (100 c.c.) was added. (Note: The 4-cyano-fluoranthene was very insoluble in cold ether). The 'addition compound' formed immediately without any refluxing and was worked up as detailed above, yielding a yellow solid (0.67 g.), M.P. 103-110°C. This was dissolved in benzene and chromatographed on a column of alumina (24" long x 0.86" diameter). The solid was adsorbed as a yellow band and was eluted from a blue fluorescent impurity with benzene. Only the yellow coloured eluate was investigated, yielding a yellow solid (0.63 g.), M.P. 117-121°C. A mixed M.P. with 4-cyano-fluoranthene gave no depression, showing that the reaction had not taken place.

Preparation/

Preparation of 4-benzoyl-fluoranthene from 4-cyano-fluoranthene.

The Grignard reagent was prepared as before. The 4-cyano-fluoranthene (0.63 g.) recovered from the last attempt was dissolved in anhydrous benzene (25 c.c.) and added to the Grignard reagent. The mixture was refluxed for 10 hours when a slightly green fluorescent solution remained. This was decomposed and worked up as detailed above, giving an orange-yellow oily solid which was crystallised from alcohol giving a yellow solid, M.P. 125-129°C. A mixed M.P. with 4-cyano-fluoranthene gave a definite depression. The crude material was dissolved in benzene and chromatographed on a column of alumina (12" long x 0.86" diameter). On development with benzene a little blue fluorescent material was eluted. This was not investigated further. This was followed by a broad band of yellow fluorescent material which was eluted in two fractions. The fractions were worked up in the usual way and yielded a yellow solid which was crystallised from alcohol. Yellow needles, M.P. 129-130°C. Mixed melting points showed that this was identical with the high melting benzoyl-fluoranthene isomer isolated from the Friedel-Crafts reaction (p. 46) and the Perrier modification of the Friedel-Crafts reaction (p. 38).

Yield of crystallised material = 0.37 g. ≡ 43.8% Th.

Phthaloylation/

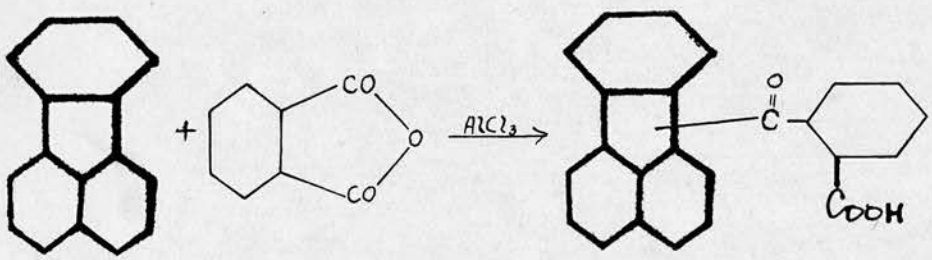
Phthaloylation of Fluoranthene.

von Braun and Manz. Annalen, 1932, 496, 186.

Fluoranthene (20 g.), phthalic anhydride (16.3 g.) and powdered aluminium chloride (33.4 g.) were refluxed together in carbon disulphide (155 c.c.) for 60 hours with agitation. The complex was decomposed with ice/water and the carbon disulphide distilled off on the water bath. Ten per cent. caustic soda solution was added until the liquor was alkaline and the sodium salt solution of the organic acid filtered. The free acid was obtained by acidifying the sodium salt solution with hydrochloric acid and filtering.

Yield = 14 g. ≡ 40.4%. Th.

Equation for the Reaction.



O-CARBOXYBENZOYL-FLUORANTHENE.

An attempt was made to prepare the picrate from the crude solid (0.3 g.) using boiling alcoholic solutions (Campbell, p. 84). This was not successful and picric acid was returned unchanged. The crude solid was rather difficultly soluble in alcohol.

An unsuccessful attempt was made to purify the crude acid by fractional crystallisation from chloroform (cf. von Braun).

The crude solid was completely dissolved in chloroform and left to crystallise. Solid (5 g.) separated out on standing. M.P. 203-214°C (fraction A). The mother liquor was evaporated completely, leaving a resinous solid (7 g.), M.P. 158-185°C. (fraction B).

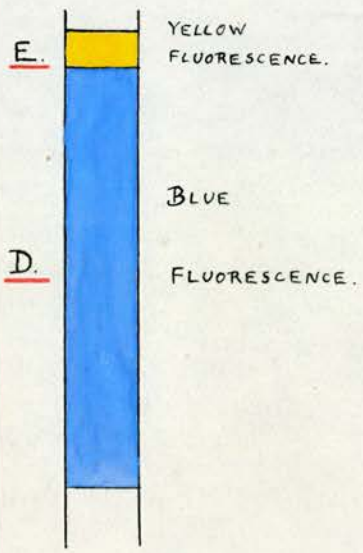
An attempt was made to chromatograph fraction A solid (0.10 g.) on a column of alumina (4" long x 0.4" diameter) using benzene as solvent. It was found that the solid was immediately adsorbed as a very narrow yellow band which could not be removed with the strongest developing agent.

Conversion of fraction A acid into the methyl ester.

The crude acid (4.5 g.) was refluxed for one hour with methyl alcohol (100 c.c.) and concentrated sulphuric acid (10 c.c.). The ester was precipitated as an oily solid by addition of water, filtered off and washed free from mineral acid. Unchanged organic acid was/

was removed by boiling with sodium carbonate solution. A small amount of crude acid (0.07 g.), M.P. 120-140°C. was recovered. The resultant ester was obviously impure and had a M.P. 100-145°C.

An attempt was made to purify the ester by chromatographic analysis. The crude ester (0.10 g.) was dissolved in benzene and chromatographed on a column of alumina (4.5" long x 0.4" diameter). The solid was adsorbed as a yellow band and developed with benzene. A blue fluorescence emerged from the yellow band and was eluted. This was followed by the visible yellow band which was also eluted leaving a blue fluorescent material on the column with a narrow yellow band near the top. The column was then washed through with alcohol so that this second yellow band could be collected. Fractions were collected as shown below and each worked up in the usual way.



A. First blue fluorescent material.

This gave nothing definite.

B. /

B. Visible and fluorescent yellow band eluted with benzene.

This gave an oil which was triturated with ether to a light yellow solid, M.P. 99-105°C. This was crystallised from light petroleum (80-100°) giving a solid, M.P. 100-103°C.

C. A cut between the yellow band and the blue fluorescence remaining on the column.

This gave an oily solid which was triturated with ether to an almost white solid, M.P. 157-168°C. This was crystallised from a mixture of light petroleum (100-120°) and a little benzene, giving solid, M.P. 173.5-175.5°C.

D. The bulk of the blue fluorescent material on the column.

This gave clusters of needle crystals, M.P. 165-171°C.

E. The narrow yellow band eluted with alcohol.

This gave dark yellow solid, M.P. 155-166°C.

F. The drainings of the column.

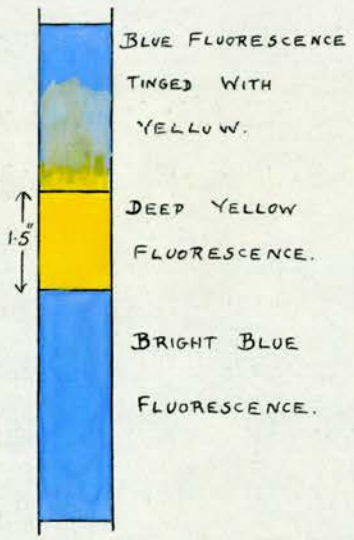
This gave a little dark orange solid of indefinite M.P.

Recovery from the column. The column was not carried through on a quantitative basis.

Conclusion: The experiment showed the possibility of separating the crude ester into two pure isomers.

The crude methyl ester of the keto-carboxylic acid/

acid (2.0 g.) was dissolved in the minimum volume of cold benzene and chromatographed in bulk on a column (24" long x 0.86" diameter). When the solid was completely adsorbed the column appeared as uniformly yellow in daylight but under the ultra-violet lamp it appeared as shown in the accompanying diagram. The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°). The blue fluorescence at the bottom of the column was eluted. The deep yellow band broadened, moved slowly down the column and was eluted with a 1:1 mixture of benzene and light petroleum (80-100°), leaving the column uniformly blue. The blue fluorescent material was finally eluted with alcohol. Fractions were collected as shown below and worked up in the usual way.



A. Blue fluorescent material eluted from the column.

This gave 0.09 g. pale-yellow oily solid, M.P. 68-85°C. which was not purified further.

B. A cut between the blue and deep yellow fluorescent bands.

This gave 0.10 g. dark yellow solid, M.P. 81-98°C. which/

which was crystallised from light petroleum (100-120°) giving yellow crystals, M.P. 100-102°C.

C. First fraction of deep yellow eluate.

D. Second fraction of deep yellow eluate.

These fractions gave 0.60 g. fluffy yellow crystals, M.P. 97-104°C., which were crystallised from light petroleum (100-120°) yielding yellow crystals, M.P. 103.5-105°C. This substance was analysed for the methyl ester of o-carboxybenzoyl-fluoranthene as follows:-

$C_{25}H_{16}O_3$ requires C, 82.41%; H, 4.39%.

found C, 82.66%; H, 4.64%.

E. A cut between the yellow band and the blue fluorescent material remaining on the column.

F. Main fraction of blue fluorescent material.

These fractions gave 0.40 g. yellow crystalline solid, M.P. 134-145°C., which was crystallised from light petroleum (100-120°) giving yellow crystals, M.P. 168-170°C. A little of this material was re-crystallised from light petroleum (100-120°). This gave material M.P. 172-173.5°C. which was analysed for the methyl ester of o-carboxybenzoyl-fluoranthene as follows:-

$C_{25}H_{16}O_3$ requires C, 82.41%; H, 4.39%.

found C, 80.79%; H, 4.48%.

G./

G. Alcoholic eluate from the column.

This gave 0.25 g. orange-yellow solid, M.P. 145-161°C., which was crystallised from light petroleum (100-120°) giving yellow crystals, M.P. 164-170°C.

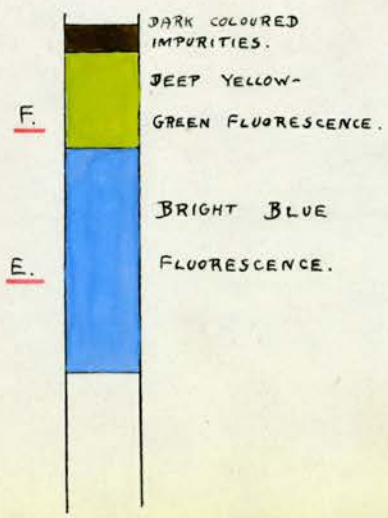
Recovery from the column = 1.44 g. ≡ 72.0% Th.

Conclusion:- This column showed the presence of two isomers in approximately equal amounts in the crude methyl ester of o-carboxybenzoyl-fluoranthene.

Conversion of fraction B acid into the methyl ester.

The crude acid (7.0 g.) was treated as detailed for fraction A acid (p.67), yielding a dark orange oil (5.0 g.) which would not solidify even after prolonged trituration with alcohol.

The crude oil was dissolved in the minimum quantity of cold benzene and chromatographed on a column of alumina (24" long x 0.86" diameter). The solid was adsorbed as a yellow band with dark coloured impurities at the top and a blue fluorescence emerging from the bottom. The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°) when the blue fluorescent material was eluted, followed by the deep yellow band. The column then appeared under the ultra-violet lamp as shown in the accompanying diagram.



The/

The column was drained and cut into sections as shown. Each section of the column of alumina was extracted with boiling alcohol. The various fractions were worked up in the usual way.

A. Blue fluorescent material eluted from the column.

This gave an oily orange solid (0.21 g.) which would not solidify even on prolonged trituration with alcohol. This was not investigated further.

B. A cut between the blue and deep-yellow fluorescent bands.

This gave an oily solid similar to fraction A (0.13 g.).

C. Deep yellow eluate.

This gave an oil which changed to a deep yellow solid (1.15 g.) on trituration with ether, M.P. 87-99°C. This material was crystallised from a mixture of benzene and light petroleum (80-100°) giving clusters of yellow needles, M.P. 101-103°C. A mixed M.P. with the corresponding material from fraction A acid gave no depression.

D. The benzene/light petroleum eluate of the blue fluorescence and drainings of the column.

This gave an oil (1.40 g.) which solidified to an orange solid on trituration with ether, M.P. 101-148°C. This was crystallised from a mixture of benzene and light/

light petroleum (80-100°) giving a solid of M.P. 144-160°C.

E. Lower part of the column extracted with alcohol.

This gave 0.10 g. orange solid, M.P. 110-155°C.

F. Upper part of the column extracted with alcohol.

This gave 0.22 g. orange solid, M.P. 120-160°C.

Recovery from column = 3.21 g. ≡ 64.2% Th.

Conclusion: The column gave a partial separation of the crude ester from fraction B acid and showed the presence of one ester corresponding to that obtained from fraction A acid.

The crystallised material from fraction D of the last column (1.08 g.) was rechromatographed on a column of alumina (14.5" long x 0.86" diameter) with benzene as solvent. The solid was adsorbed as a yellow band and developed with a 4:1 mixture of benzene and light petroleum (80-100°) when a pale yellow band moved down the column and was eluted, leaving the column uniformly blue under the ultra-violet lamp. Fractions were collected as shown below and worked up in the usual way.

A. Yellow band as followed under the ultra-violet lamp.

This gave 0.13 g. yellow oil which was triturated with ether to a yellow solid, M.P. 80-102°C.

This/

This was crystallised from a mixture of benzene and light petroleum (80-100°) giving yellow needles, M.P. 102-105°C. A mixed M.P. with the corresponding ester from fraction A acid gave no depression.

B. First fraction of the blue fluorescent material eluted with the benzene/light petroleum mixture.

This gave 0.17 g. oily solid, M.P. 96-140°C. which was crystallised from a mixture of benzene and light petroleum (80-100°) giving a yellow crystalline solid, M.P. 166-169°C.

C. Second fraction of the blue fluorescent material eluted with alcohol.

This gave 0.59 g. oily solid, M.P. 90-160°C.

D. A narrow yellow band which developed and was eluted with alcohol.

This gave 0.10 g. orange solid, M.P. 116-162°C.

Fractions C and D were crystallised together from a mixture of benzene and light petroleum (80-100°) giving a yellow crystalline solid, M.P. 163-167°C.

Mixed M.Ps. with fractions C and (D + E) crystallised and the corresponding material obtained from fraction A acid gave no depressions.

Recovery from the column = 0.99 g. ≡ 91.7% Th.

The material from fractions E and F of the first chromatographic analysis (p. 72) (0.32 g.) was re-chromatographed/

chromatographed on a column of alumina (8.5" long x 0.63" diameter) using benzene as solvent. The column was developed with a 4:1 mixture of benzene and light petroleum (80-100°) and a yellow fluorescent material eluted from the column. The column appeared under the ultra-violet lamp as shown in the accompanying diagram. The column was drained and the alumina cut into sections as shown. The various fractions were worked up in the usual way.

A. Yellow band eluted with benzene/light petroleum.

This gave an orange solid of very indefinite M.P. over a long range up to 120°C.

B. Dark band on column extracted with boiling alcohol.

This gave a dark orange solid which did not melt below 320°C.

C. Second yellow band extracted with alcohol.

This gave a dark solid of very indefinite M.P. over a long range to 230°C.

Recovery: The column was not carried through on a quantitative basis.

These fractions were not investigated further (a) in view of the small amount of material involved in

a /

a relatively large preparation, (b) they were obviously not the two isomeric esters around which this investigation chiefly centred.

Conclusion:- Fractional crystallisation of the crude acid followed by esterification of each fraction and chromatographic analysis showed the presence of two isomeric o-carboxybenzoyl-fluoranthenes in approximately equal quantities.

Hydrolysis of the low M.P. methyl ester of o-carboxybenzoyl-fluoranthene.

The ester (0.40 g.) was refluxed for half an hour with 10% sodium hydroxide solution (10 c.c.). Dilute hydrochloric acid was added and the crude acid (0.30 g.) filtered off and washed free from mineral acid. The crude acid was crystallised from a mixture of glacial acetic acid and a little alcohol. On addition of a little water yellow needle-prisms were obtained, M.P. 216-224°C. This material was further crystallised from glacial acetic acid giving bright yellow needle-prisms, M.P. 231-232°C. This was analysed for o-carboxybenzoyl-fluoranthene as follows:-

Calc. for $C_{24}H_{13}O_3$ C, 82.28%; H, 4.00%.

found C, 81.66%; H, 4.09%.

Yield of crude acid ≡ 78.0% Th.

Decarboxylation/

Decarboxylation of keto-carboxylic acid

The acid obtained from the previous hydrolysis (0.05 g.) was heated in quinoline with a pinch of copper bronze. Frothing occurred at 195°C. and the reaction was complete after 10 minutes at this temperature. The quinoline solution was now strongly fluorescent. The mixture was decomposed with dilute hydrochloric acid, the solid filtered and washed free from mineral acid. The solid was dissolved in benzene, dried over anhydrous calcium chloride and chromatographed on a column of alumina (3.75" long x 0.4" diameter). Some dark tarry material was adsorbed at the top of the column and a pale yellow band moved down on development with a 3:1 mixture of benzene and light petroleum (80-100°). The yellow band was eluted and worked up in the usual way yielding a yellow solid M.P. 122-125°C. This was crystallised from alcohol and gave yellow needles, M.P. 129-130°C. A mixed M.P. with 4-benzoyl-fluoranthene gave no depression proving that the low melting point methyl ester of o-carboxybenzoyl-fluoranthene and the acid obtained from it are the 4- substituted derivatives.

Preparation/

Preparation of oxime of 4-o-carboxybenzoyl-fluoranthene

This was prepared as detailed on p.51 using 0.05 g. acid. The crude solid was crystallised from benzene giving clusters of almost colourless needles, M.P. 221-225°C. with charring.

Analysis: $C_{24}H_{15}O_3N$ requires N, 3.83%.

found N, 3.60%.

Hydrolysis of high M.P. methyl ester of o-carboxybenzoyl-fluoranthene.

The ester (0.30 g.) was refluxed with 10% caustic soda solution (10 c.c.) and alcohol (10 c.c.) for 4 hours. The hydrolysis was more difficult to effect than with the low M.P. isomeric ester. Dilute hydrochloric acid was added, the crude acid filtered off and washed free from mineral acid. The crude acid (0.20 g.) was crystallised from glacial acetic acid, M.P. 224-229°C. A little of this material was recrystallised from glacial acetic acid, M.P. 227-228°C. and analysed for o-carboxybenzoyl-fluoranthene as follows:-

$C_{24}H_{14}O_3$ requires C, 82.28%; H, 4.00%.

found C, 82.39%; H, 4.03%.

A mixed M.P. with 4-o-carboxybenzoyl-fluoranthene was 208-223°C., showing a definite depression.

Yield of crude acid = 69.3% Th.

Decarboxylation/

Decarboxylation of keto-carboxylic acid

This was done as described for the 4-isomer on p.78 using the acid obtained from the last hydrolysis (0.05 g.). The reaction was complete after 20 minutes at 175-180°C. The crude acid was dissolved in benzene, dried over anhydrous calcium chloride and chromatographed on a column of alumina (3.5" long x 0.40" diameter). Some tarry residue was adsorbed at the top of the column. Below this a blue fluorescent band developed which was eluted with alcohol, and worked up in the usual way. This yielded a solid which was crystallised from alcohol giving colourless plates which fluoresced blue under the ultra-violet lamp, M.P. 117-119°C. A mixed M.P. with 11-benzoyl-fluoranthene gave no depression showing that the high melting point methyl ester of o-carboxybenzoyl-fluoranthene and the corresponding acid are the 11-substituted derivatives.

Preparation of oxime of 11-o-carboxybenzoyl-fluoranthene

This was prepared as detailed on p. 51 using 0.05 g. acid. The crude oxime, M.P. 223-228°C. with charring, (mixed M.P. with the original keto-acid was 193-212°C.) was crystallised from benzene giving compact prism crystals which were slightly brown,

M.P./

M.P. 232-235°C. with sublimation. A mixed M.P. with the oxime of 4-o-carboxybenzoyl-fluoranthene gave a depression (214-223°C.).

Analysis: $C_{24}H_{15}O_3N$ requires N, 3.83%.

found N, 7.06%.

Since the analysis of the 11-substituted carboxylic acid was in agreement with theoretical it seems reasonable to suspect a faulty analysis here. Correspondence with Drs. Weiler and Strauss failed to reveal any error and there was insufficient material for a repeat analysis.

Decarboxylation of anthraquinone carboxylic acids.

In working out the technique for the decarboxylations described above, preliminary experiments were done using anthraquinone carboxylic acids. Under the conditions described, it was found that anthraquinone-1-carboxylic acid was easily decarboxylated to anthraquinone, while the 2-substituted isomer was not.

Fluoranthene Carboxylic Acids.

Preparation of anhydrous oxalic acid from oxalic acid dihydrate.

Thionyl chloride (40 g. ≡ 100% excess) was added dropwise to powdered crystalline oxalic acid (10 g.). The mixture was refluxed on the water-bath for half an/

an hour during which time there was a vigorous reaction. The gases evolved were trapped in cooled caustic soda solution. The excess thionyl chloride was distilled off under vacuum leaving a fine white solid (6.0 g.), M.P. 189°C., sharp.

Yield = 84.5% Th.

Attempted preparation of oxalyl-chloride

Thionyl chloride (396 g. ≡ 50% excess) was added dropwise to anhydrous oxalic acid (100 g.). The mixture was refluxed on the water bath for 12 hours after which time it appeared as a partly charred mass. The liquid remaining was filtered off from the black mass and fractionally distilled. Unchanged thionyl chloride was recovered but there was no indication of any oxalyl-chloride.

Preparation of oxalyl-chloride.

Anhydrous oxalic acid (90 g.) was intimately mixed with powdered phosphorus pentachloride (400 g.) and left in a flask fitted with a calcium chloride tube for 3 days. A very slow reaction ensued with evolution of hydrochloric acid gas. The liquid was decanted from the little remaining solid and purified by repeated fractional distillation to give oxalyl chloride (38 g.), B.P. 62-64°C.

Yield = 29.9% Th.

Preparation/

Preparation of fluoranthene carboxylic acids.

von Braun and co-workers. Annalen, 1932, 496, 178.

Powdered aluminium chloride (6.5 g.) was added to fluoranthene (9 g.) in carbon disulphide (70 c.c.) and agitated. Oxalyl chloride (17 g.) was added dropwise over one and a half hours. During the addition the mass became very sticky and difficult to agitate but towards the end of the addition it became friable again and therefore more easily agitated. The mixture was stirred for 18 hours in an ice-bath when more powdered aluminium chloride (13 g.) and carbon disulphide (100 c.c.) were added. Stirring was continued for 2 days at 0°C. and for a day longer at room temperature.

The reaction mixture was decomposed with ice-cold dilute hydrochloric acid. The carbon disulphide was distilled off on the water-bath, leaving a greenish-brown mass. This was filtered and washed well with water until free from mineral acid. The filtrate was discarded. The brown mass remaining was boiled with excess sodium carbonate solution to extract the carboxylic acids present. The alkaline solution was filtered and acidified with dilute hydrochloric acid, yielding a thixotropic mass which was difficult to filter. The paste was washed free from mineral acid and dried.

Conversion/

Conversion of crude fluoranthene carboxylic acid to its methyl ester.

The crude solid (17 g.) was refluxed with methyl alcohol (350 c.c.) and concentrated sulphuric acid (35 c.c.) for one hour. The bulk of the solid did not dissolve. The solid residue (10 g.) was filtered off. The bulk of the methanol was distilled off and the oily residue poured into water. An oil separated which was extracted with ether. The ether layer was washed with water, sodium carbonate solution (crude acid (1 g.) m.p. 217-250°C. recovered) and finally twice with water. The ethereal solution was dried over anhydrous sodium sulphate and the ether distilled off, leaving a yellow solid (1.75 g.) M.P. 75-90°C. (Fraction A ester).

A further attempt was made to esterify the residue and recovered acid from the last esterification. The crude residue (11 g.) was refluxed for 4 hours with methyl alcohol (220 c.c.) and concentrated sulphuric acid (22 c.c.). The ester was worked up as detailed for the first trial and yielded a yellow solid (3.38 g.) (Fraction B ester).

Yield of crude ester = 46.8% Th. from fluoranthene

Fraction A ester was chromatographed on a column of alumina (24.5" long x 0.86" diameter) with benzene as solvent. The crude ester was adsorbed as a broad yellow/

yellow band and the column was developed with a 3:1 mixture of benzene and light petroleum (80-100°C.). Two separate yellow bands developed on a blue fluorescent background. The lower yellow band was eluted and then the column further developed with 5 drops alcohol per 100 c.c. mixed solvent. On final development with alcohol alone, the top yellow band divided and elution was carefully followed so that these bands were collected separately. Fractions were collected as shown below and each was worked up in the usual way.

A. First fraction of lower yellow band eluted with benzene and light petroleum.

This gave a yellow solid (0.20 g.), M.P. 61-65°C. which was crystallised from alcohol, M.P. 64-69°C.

B. Second fraction of lower yellow band eluted with benzene/light petroleum.

This gave a yellow solid (1.05 g.), M.P. 90-93°C. which was crystallised from alcohol, M.P. 93-95°C. This material was analysed for the methyl ester of fluoranthene-carboxylic acid as follows:-

$C_{18}H_{12}O_2$ requires C, 83.08%; H, 4.61%.
found C, 82.33%; H, 4.90%.

C. Fraction of eluate from development with 100 c.c. benzene/light petroleum/alcohol.

This gave a yellow solid (0.08 g.), M.P.78-84°C. which/

which was crystallised from alcohol, M.P. 79-86°C. Nothing further was done on this material.

D. Eluate collected till second yellow band reached the foot of the column.

This gave an oily solid (0.07 g.) melting over a large range below 100°C. Nothing further was done on this material.

E. Second yellow band eluted separately.

This gave a yellow solid (0.13 g.), M.P. 134-142°C. which was crystallised from alcohol giving yellow crystals, M.P. 145-148°C. This substance was analysed for the methyl ester of fluoranthene-carboxylic acid as follows:-

$C_{18}H_{12}O_2$ requires C, 83.08%; H, 4.61%.
found C, 72.26%; H, 4.44%.

The substance was obviously not a mono-carboxylic ester but the analysis agreed with the theoretical for a dicarboxylic ester as shown below.

$C_{20}H_{14}O_4$ requires C, 75.5%; H, 4.40%.
found C, 72.26%; H, 4.44%.

second
A/crop of crude crystals was obtained from the alcoholic mother liquor on standing, M.P. 111-132°C.

F. Final alcoholic washings from the column.

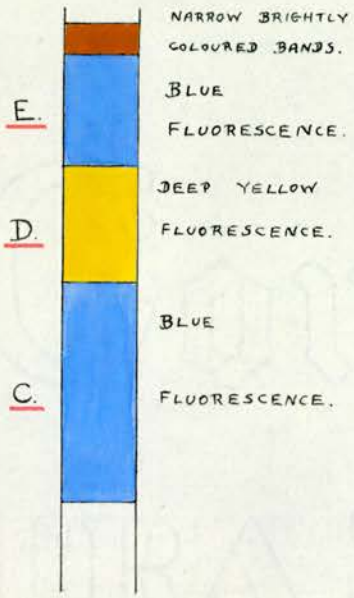
This gave a very small fraction of dark yellow solid, M.P. 174-178°C. Nothing further could be done with this substance.

Recovery from column = 1.53 g. ≡ 87.5% Th.

Conclusion/

Conclusion: Chromatographic separation showed the presence of a mono- and a di-carboxylic ester in Fraction A of the crude ester.

Fraction B ester was chromatographed on a column of alumina (25" long x 0.86" diameter) with benzene as solvent. The solid was adsorbed as a broad uniformly yellow band. The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°). The lower yellow band was completely eluted after which the column appeared under the ultra-violet lamp as shown in the accompanying diagram. The column was drained, the alumina extruded and cut into sections as shown.



Each section of the column was extracted with boiling alcohol and the various fractions worked up in the usual way.

A. First fraction of first yellow band eluted from the column.

This gave a pale yellow solid (0.97 g.), M.P. 81-90°C. which was crystallised from alcohol, M.P.89-92°C.

B. /

B. Second fraction collected until the yellow band was eluted completely.

This gave an almost colourless solid (0.56 g.), M.P. 90-95°C. which was crystallised from alcohol, M.P. 94-96°C.

C. The blue fluorescent material left at the bottom of the column.

This gave a deep yellow solid (0.04 g.), M.P. 65-115°C. An attempt was made to crystallise this material from alcohol, M.P. 145-158°C. with slow sintering. Nothing further was done with this small amount of material.

D. The deep yellow fluorescent band.

A deep yellow solid (0.50 g.) separated from the alcoholic extract before concentrating. This was filtered off, M.P. 178-181°C. This material was crystallised from alcohol giving a substance, M.P. 183-184.5°C. which was analysed for the methyl ester of fluoranthene carboxylic acid as follows:-

$C_{20}H_{14}O_4$ requires C, 75.5; H, 4.40%.

found C, 75.3%; H, 4.60%.

This proved that the substance was the methyl ester of a fluoranthene dicarboxylic acid.

Concentration of the alcoholic mother liquor gave a further 0.70 g. of deep yellow solid, M.P. 137-155°C. which was crystallised from alcohol,

M.P./

M.P. 155-170°C. This material was not purified further.

E. The blue fluorescent material extracted from the top of the column.

This gave 0.06 g. yellow solid, M.P. 100-109°C., which was crystallised from alcohol, M.P. 110-117°C. Nothing further was done with this fraction.

The material of fractions A and B of this column gave no depression when a mixed M.P. was done with the corresponding material from fraction A crude ester.

No definite conclusions were derived from a mixed M.P. with the two materials which analysed for the ester of fluoranthene-dicarboxylic acid.

Recovery from column = 2.83 g. = 83.7% Th.

Conclusion: Chromatographic analysis of fractions A and B methyl esters showed the presence of one fluoranthene-monocarboxylic acid and one fluoranthene-dicarboxylic acid in an approximate weight ratio of 2:1.

Hydrolysis of the methyl ester of fluoranthene-monocarboxylic acid.

The ester (0.95 g.) was refluxed for one hour with 10% caustic soda solution (25 c.c.) after which time the ester had dissolved completely. The crude acid/

acid was worked up in the usual way. The crude solid, M.P. 260-270°C. with charring, was crystallised from glacial acetic acid (not very soluble), giving clusters of colourless needles, M.P. 275-278°C. with darkening. The acid sublimed above 220°C.

A second crop of crystals formed on long standing, M.P. 273-278°C. This material was crystallised from glacial acetic acid, giving a solid, M.P. 278-280°C. which was analysed for fluoranthene-monocarboxylic acid as shown below:-

$C_{17}H_{10}O_2$ requires C, 82.9%; H, 4.06%.

found C, 81.4%; H, 4.42%.

Attempt to hydrolyse the methyl ester of fluoranthene-dicarboxylic acid obtained in chromatographing fraction A ester.

The ester (0.015 g.), M.P. 145-148°C. was refluxed with 10% sodium hydroxide solution (2 c.c.) for one hour. The ester had not gone into solution by this time so alcohol (5 c.c.) was added and the whole refluxed for two and a half hours longer. The crude acid was obtained in the usual way. An attempt was made to crystallise the crude acid from glacial acetic acid but it was found to be very insoluble. After boiling in glacial acetic acid, however, the acid was much cleaner in appearance. A micro sublimation of this acid was carried out. Sublimation occurred at 310°/

310°C. giving deep-yellow needle-prisms which did not melt below 350°C. The exact M.P. was not determined and there was not sufficient material for analysis.

Attempt to hydrolyse the methyl ester of fluoranthene-dicarboxylic acid obtained in chromatographing fraction B ester.

The ester (0.45 g.), M.P. 183-184.5°C., was refluxed with 10% caustic soda solution (20 c.c.) for 3 hours after which time all the solid had gone into solution. The crude acid was worked up in the usual way. A micro sublimation of the crude acid gave yellow needle prisms from 260°C. which did not melt below 350°C. The exact melting-point was not determined.

A little of the crude acid was boiled with glacial acetic acid, in which it was practically insoluble, the residue filtered off, dried and analysed for fluoranthene-dicarboxylic acid as follows:-

3.679 mg. $\longrightarrow$ 9.220 mg. CO_2, 1.300 mg. H_2O and 0.228 mg. residue.

$C_{18}H_{10}O_4$ requires C, 74.5%; H, 3.45%.
found C, 72.9%; H, 4.18%.

The analysis figures were calculated assuming that the residue was uncombusted material.

A comparative micro-sublimation was carried out with the two acids, obtained from the hydrolyses above, side by side on the same slide. This showed that/

that they were probably identical, sublimation commencing at 266°C. in each case and each acid depositing yellow needle-prisms which did not melt below 350°C.

Hydrolysis of 4-cyano-fluoranthene to fluoranthene-4-carboxylic acid.

von Braun and coworkers. Annalen, 1931, 488,119.

In the first attempt to effect hydrolysis 4-cyano-fluoranthene (0.12 g.) was heated in a sealed tube with concentrated hydrochloric acid (1.2 g.) for 18 hours at 130°C. Unchanged 4-cyano-fluoranthene was recovered (m.p. and mixed m.p.).

In a further attempt, the recovered 4-cyano-fluoranthene was heated in a sealed tube with concentrated hydrochloric acid (10 c.c.) for 16 hours at 200°C. The mixture was filtered and washed free from mineral acid. The solid was extracted with boiling sodium hydroxide solution and filtered. The crude acid was precipitated from the sodium salt solution with dilute hydrochloric acid, M.P. 253-257°C. with sublimation. A micro sublimation was done on a little of the crude material. 'Sweating' occurred from 150°C., giving droplets of liquid which crystallised into clusters of bright yellow needles at 230-240°C. The M.P. of the sublimed material was

283/

283-285°C. with slight decomposition.

The bulk of the crude acid was crystallised from glacial acetic acid giving a yellow crystalline material, M.P. 281-286°C. with darkening. This was analysed for fluoranthene-4-carboxylic acid as follows:-

Calc. for $C_{17}H_{10}O_2$ C, 82.9%; H, 4.06%.

found C, 79.27%; H, 3.71%.

A mixed M.P. was done with the sublimed acid and the monocarboxylic acid obtained in the Friedel-Crafts reaction (M.P. 278-280°C.). This gave a definite depression (243-255°C.) indicating that the acid obtained in the Friedel-Crafts reaction was probably fluoranthene-11-carboxylic acid.

Decarboxylation of fluoranthene-4-carboxylic acid.

The acid (0.02 g.) was heated with a little copper bronze in quinoline. A brisk reaction was seen to occur at 200-205°C. and was complete after 20 minutes at this temperature. The quinoline solution was now strongly fluorescent. The mixture was decomposed with dilute hydrochloric acid and the solid separated by centrifuging. A micro sublimation was done on the crude paste giving white needles which fluoresced blue under the ultra-violet lamp, M.P. 109-110°C. A mixed M.P. with fluoranthene gave no depression/

depression.

Attempt to decarboxylate fluoranthene-11-carboxylic acid.

The acid (0.05 g.) was heated in quinoline, with a little copper bronze, to 235°C. and maintained at this temperature for half an hour. No visible reaction occurred. The quinoline mixture was worked up as described above. A micro sublimation of the crude solid gave clusters of colourless needle-shaped crystals, M.P. 270-277°C. A mixed M.P. with the starting material gave no depression, indicating that no reaction had occurred.

Attempt to decarboxylate fluoranthene-dicarboxylic acid.

The acid (0.05 g.) was heated in quinoline with a little copper bronze. A vigorous reaction occurred at 220°C. and was complete in half an hour. The quinoline mixture was worked up in the usual way. A micro sublimation gave (a) at 90°C. a small amount of colourless needles which fluoresced blue under the ultra-violet lamp, M.P. and mixed M.P. showed this to be fluoranthene, (b) 'sweating' from 180°C. which ultimately gave almost colourless needle-crystals, M.P. 276-279°C. A mixed M.P. with fluoranthene-11-carboxylic acid gave no depression.

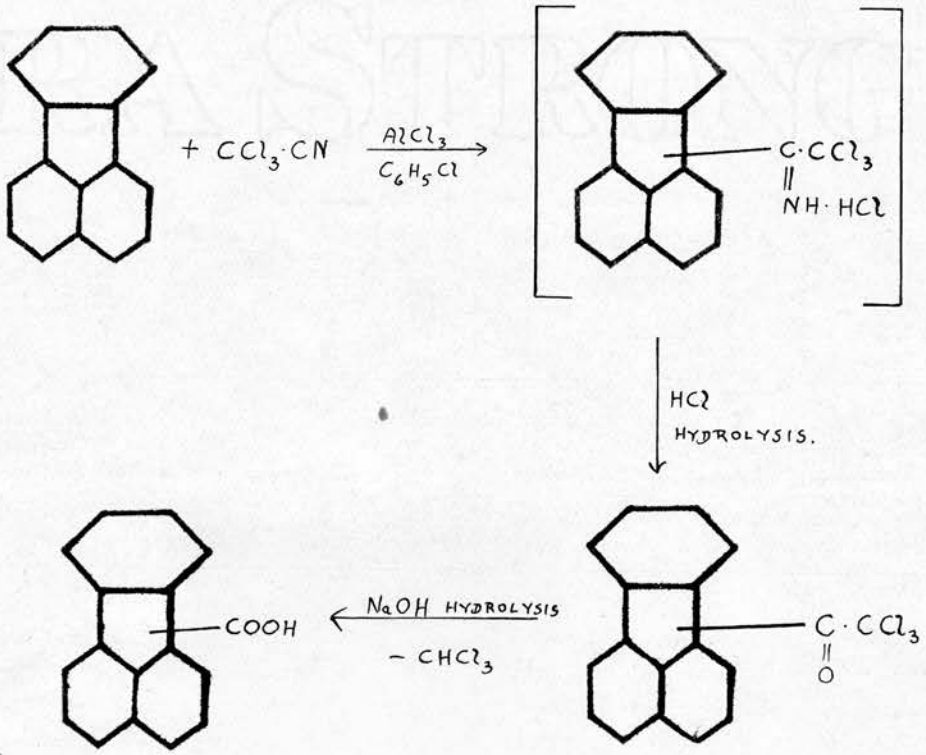
This would indicate that the very high M.P. dicarboxylic/

dicarboxylic acid was really a mixture of (a) fluoranthene-4-carboxylic acid in small quantity and (b) fluoranthene-4:11-dicarboxylic acid. It was interesting to note that this was the only evidence of fluoranthene-4-carboxylic acid having been present in the mixture although von Braun claimed to have handled it in bulk.

Preparation of fluoranthene-carboxylic acids by the Houben reaction.

Dunlop and Tucker, J.C.S.,1939, 1953.

Equation for reaction:



Preparation of ethyl-trichloracetate.

Dry hydrochloric acid gas was passed into trichloracetic acid (82 g.) in alcohol (23 g.) for 5 hours with ice-cooling. The whole was then poured into water and the ester extracted with ether. The ether layer was washed with sodium carbonate solution, then with water and finally dried over anhydrous sodium sulphate. The ether was distilled off and the remaining oil fractionally distilled, B.P.164-166°C.

Yield = 66 g. ≡ 68.7% Th.

(cf. Tucker: yield ≡ 90% Th.,B.P. 167.1°C./754.8 mm.)

Preparation of trichloracetamide

Ethyl trichloracetate (66 g.) was shaken thoroughly in a stoppered flask with excess concentrated ammonia. The solid amide separated in fine white plates after 15 minutes shaking, M.P. 139-141°C.

Yield = 43 g. ≡ 76.8% Th. (cf. Tucker: yield ≡ 60% Th.)

Preparation of trichloracetonitrile

Trichloracetamide (43 g.) was intimately mixed with phosphorus pentoxide (70 g.) and heated under gentle reflux for one and a half hours. The crude trichloracetonitrile was distilled off and fractionally distilled, B.P. 84-86°C.

Yield = 23 g. ≡ 60.1% Th. (cf. Tucker: yield ≡ 80%)

Preparation/

Preparation of fluoranthene-carboxylic acids

Fluoranthene (20 g.) and trichloracetonitrile (17.4 g.) were shaken together in chlorobenzene (160 c.c.) and aluminium chloride (16 g.) gradually added. The mixture was then saturated with hydrochloric acid gas. The temperature was raised to 100°C. over an hour and maintained at 100°C. for one hour with frequent shaking.

The resultant product was decomposed with excess concentrated hydrochloric acid and the chlorobenzene removed by steam distillation leaving a dark red solid. The solid was further treated with concentrated hydrochloric acid, filtered off and washed free from mineral acid. The crude solid was then treated with excess caustic soda solution and heated, when chloroform was evolved.

The sodium salt liquor of the fluoranthene carboxylic acids was filtered leaving a dark muddy sludge. Filtration was slow and difficult. The liquor was acidified with hydrochloric acid and the crude brown acid filtered, washed and dried.

Fraction I acid; 20 g.

The sludge from the sodium salt liquor was thoroughly washed with boiling water until the filtrate was quite colourless. This operation was very prolonged because of the bad filtering state of the sludge/

sludge. The wash liquor was acidified.

Fraction II acid; 12 g.

The black residue which remained was dried (20 g.). A micro sublimation was done on this residue and gave 'sweating' from 200°C. upwards. Yellow globules of liquid appeared which did not really solidify but there were signs of 'increased mobility' at 310°C. This was very indefinite. The sublimate was treated with a drop of concentrated hydrochloric acid and the excess volatilised. There was no apparent change in the melting-point observations from those already described.

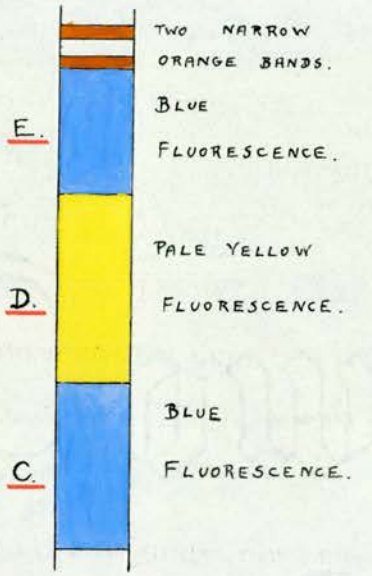
Esterification of fraction I acid.

The crude acid (20 g.) was refluxed with methyl alcohol (400 c.c.) and concentrated sulphuric acid (40 c.c.) for 5 hours giving a yellow solution and a small amount of black residue (1.37 g.) which was removed by filtration. The ester was worked up in the usual way by diluting into water and extracting with ether. A pale yellow solid resulted.

Yield = 5 g. ≡ 19.9% Th. from fluoranthene.

The crude ester was chromatographed on a column of alumina (20.5" long x 0.86" diameter) with benzene as solvent. The solid was adsorbed as a yellow band (6" long) at the top of the column. On development with/

with a 3:1 mixture of benzene and light petroleum (80-100°) the yellow band was washed down the column and was eluted completely. The column then appeared under the ultra-violet lamp as shown in the accompanying diagram. The column of alumina was extruded and cut as shown. Each section was extracted with boiling alcohol and the various fractions worked up in the usual way.



A. Yellow band which was eluted with mixed solvent.

This gave a yellow solid (3.78 g.), M.P. 72-85°C. which was crystallised from alcohol, M.P. 87-92°C. A little of this material was recrystallised from alcohol giving clusters of very pale yellow needles, M.P. 96-97°C. A mixed M.P. with the corresponding ester from the Friedel-Crafts reaction (p. 85) M.P. 93-95°C. gave no depression.

B. The benzene/light petroleum drainings from the column.

This gave 0.08 g. pale yellow solid, M.P.89-95°C. Nothing was done to purify this further.

C. The blue fluorescent material extracted from the bottom of the column with alcohol.

This gave a negligible amount of a dark orange oily/

oily solid of very indefinite M.P. - a slow melting from 50-120°C.

D. The yellow band left in the column.

This gave 0.06 g. deep yellow oil which solidified on triturating with ether, M.P. 117-124°C.

E. The blue fluorescent material extracted from the top of the column with alcohol.

This gave a negligible amount of a dark oily solid with a very indefinite M.P.

Recovery from column = 4.02 g. ≡ 80.4% Th.

Conclusion: The column gave mainly one pure methyl ester of a fluoranthene carboxylic acid, which corresponds to that obtained from the Friedel-Crafts reaction with oxalyl chloride. It has also shown the presence of a trace of another methyl ester.

Hydrolysis of methyl ester obtained from fractions A and B above.

The crude ester (3.50 g.) was refluxed with 10% sodium hydroxide solution (50 c.c.) for one and a half hours after which time all the oily solid had gone into solution. The carboxylic acid was precipitated with hydrochloric acid and the resultant yellow solid filtered off. The crude acid was crystallised from glacial acetic acid and carbon-screened, giving yellow crystals, M.P. 271-278°C.

with/

with slight decomposition. There were signs of 'sweating' from 190°C. upwards.

A mixed M.P. with fluoranthene-4-carboxylic acid, M.P. 283-285°C. (p. 93), gave a definite depression. A mixed M.P. with the fluoranthene-monocarboxylic acid obtained from the Friedel-Crafts reaction, M.P. 278-280°C. (p.90), gave no depression, indicating that this acid was probably fluoranthene-11-carboxylic acid.

Yield of crystallised acid = 2.50 g. ≡ 75.5% Th.

Hydrolysis of methyl ester obtained from fraction D above.

The crude ester (0.06 g.) was refluxed with 10% sodium hydroxide solution (5 c.c.) for 5 hours. The crude acid was worked up in a similar way to that indicated above. A micro-sublimation was done on the crude acid. Sublimation started at 265°C. and the temperature was maintained at 265-275°C. for 10 minutes. A yellow solid sublimed but not in a very definite crystalline form. An attempt was made to determine the M.P. of the yellow sublimate. There was slow darkening from 190°C. upwards and the solid did not melt below 350°C.

The sublimed material was resublimed but a definite/

definite M.P. could not be obtained even on this material. It is possible that this acid corresponds to the dicarboxylic acid obtained in the Friedel-Crafts reaction (cf. p. 91).

Esterification of Fraction II crude acid.

The crude acid (12 g.) was refluxed with methanol (250 c.c.) and concentrated sulphuric acid (25 c.c.) for 5 hours. The ester was worked up exactly as detailed above under Fraction I esterification.

Yield = 4.20 g. crude ester ≡ 16.0% Th. from fluoranthene

The crude ester was chromatographed on a column of alumina (22.5" long x 0.86" diameter) with benzene as solvent. The solid was adsorbed as a yellow band (8" long) at the top of the column and was developed with a 3:1 mixture of benzene and light petroleum (80-100°). The yellow band moved slowly down the column and was eluted, leaving narrow orange bands of impurity at the top of an otherwise clear column. Fractions were collected as shown below and worked up in the usual way.

A. Mixed solvent fore-runnings of main yellow band.

This fraction was blank.

B. /

B. Main yellow band.

This gave a yellow solid (3.69 g.), M.P. 92-96°C. This was not purified further.

C. Drainings from the column.

This gave 0.03 g. solid, M.P. 97-105°C. Nothing further was done on this substance.

Recovery from column = 3.72 g. ≡ 88.6% Th.

Conclusion: Chromatographic separation effected a purification of fraction II crude ester, giving an ester, in bulk, of the same M.P. as that which was obtained from fraction I crude ester.

Attempt to esterify the residue from fractions I and II crude acid.

The residue was refluxed with methanol (400 c.c.) and concentrated sulphuric acid (40 c.c.) for 5 hours leaving a black residue (16 g.) which showed no fluorescence and was absolutely insoluble in all the common organic solvents as well as in acid and alkali. The crude acid was worked up in the usual way. The resultant ester was oily and quite different from the yellow solids obtained in the two previous esterifications.

Yield = 3.60 g. ≡ 13.7% Th. from fluoranthene.
Total yield of crude ester ≡ 49.6% Th. from fluoranthene.

The/

The crude ester (3.60 g.) was chromatographed on a column of alumina (26.5" x 0.86" diameter), with benzene as solvent. The solid was adsorbed as a yellow band and developed with a 3:1 mixture of benzene and light petroleum (80-100°). A yellow band descended the column slowly and was eluted. It was interesting to note that the side of the tube nearest the light remained yellow coloured, whilst the other side was developed until colourless. The column was colourless all round where the tube was clamped. Even after developing with alcohol one side of the tube still retained the yellow colour. Fractions were collected as shown below and worked up in the usual way.

A. Fore-runnings of yellow band.

This gave an oily scum of negligible weight.

B. Main yellow band.

This gave an oily yellow solid (2.80 g.) which was crystallised from alcohol giving a yellow solid, M.P. 105-135°C. Nothing further was done with this substance.

C. Eluate collected in an effort to develop the column until colourless.

This gave an oily scum of negligible weight.

Recovery from column = 2.80 g. ≡ 77.8% Th.

Conclusion/

Conclusion: Esterification and chromatographic analysis showed that the acid obtained from the Houben reaction consisted essentially of fluoranthene-11-carboxylic acid.

Attempted preparation of 2-benzoyl-naphthalene.

Bull. Soc. Chim. 1945, 12, 307.

Fieser's 'Experiments in Organic Chemistry',p.192.

This experiment was carried out as described in Fieser's book, p. 192 except that nitrobenzene was used as solvent in place of carbon disulphide. The Perrier addition product was prepared from benzoyl chloride (11.5 c.c.) and powdered aluminium chloride (14 g.). Nitrobenzene (80 c.c.) was added when the complex dissolved on gentle warming. Naphthalene (12.8 g.) was added slowly. Very little reaction occurred in the cold but on heating to 60°C. there was a brisk evolution of hydrochloric acid gas. The temperature was maintained at 60°C. for 20 minutes. There was no separation of solid on cooling. The mixture was poured into water and the nitrobenzene removed by steam-distillation (78 c.c. nitrobenzene recovered) leaving a dark oil. The oily/aqueous mixture was extracted with ether, the ethereal solution washed successively with water, sodium carbonate solution and water and finally dried over anhydrous calcium chloride/

chloride. The ether was distilled off leaving a dark red viscous oil which would not crystallise.

An attempt was made to purify the crude oil in ethereal solution by chromatographing on a column of alumina (21" long x 0.86" diameter). The oil was adsorbed at the top of the column as a broad red band. On developing with ether a red band moved down the column leaving a dark band of impurities to follow more slowly. The red band was completely eluted and yielded an oil (15 g.) which solidified to a greyish pink solid on 'scratching', M.P. $<70°C$. over a large range.

Preparation of 2:4-dinitrophenylhydrazone of the crude ketone.

There was no reaction with Allen's method. Unchanged 2:4-dinitrophenylhydrazine was recovered on diluting the alcoholic solution with water.

With Brady's method of formation, a solid separated from the hot solution after refluxing for half an hour. The mixture was cooled and the solid filtered, M.P. 222-234°C. with darkening. The solid was not very soluble in alcohol or glacial acetic acid. On boiling in a mixture of these solvents, the solid assumed a cleaner crystalline form of dark orange needles, M.P. 254-258°C. Some solid crystallised

from/

from the alcohol/glacial acetic acid mixture on standing, giving orange needles, M.P. 254-257°C. This was analysed for the 2:4-dinitrophenylhydrazone of benzoyl-naphthalene as follows:-

$C_{23}H_{16}O_4N_4$ requires N, 13.6%.

found N, 14.2%.

(compare Analyst, 1936, 61, 391:- 2:4-dinitrophenylhydrazone of 2-benzoyl-naphthalene, M.P. 257-258°C. with no analysis given)

Preparation of 2:4-dinitrophenylhydrazone of 2-benzoyl-naphthalene

A sample of 2-benzoyl-naphthalene prepared from 2-cyano-naphthalene was supplied by Dr Campbell. The 2:4-dinitrophenylhydrazone was formed easily by Allen's method. The crude material was boiled up with a mixture of ethyl alcohol and glacial acetic acid. The residue was filtered off. M.P. 233-235°C., and the crystallised material, which separated on cooling, M.P. 231.5-233°C., was analysed for the 2:4-dinitrophenylhydrazone of 2-benzoyl-naphthalene as follows:-

$C_{23}H_{16}O_4N_4$ requires N, 13.6%.

found N, 14.5%.

A repeat preparation of the 2:4-dinitrophenylhydrazone of 2-benzoyl-naphthalene confirmed the results and M.P. given above. A mixed M.P. was done with/

with the 2:4-dinitrophenylhydrazone prepared from the crude ketone. This was very indefinite, 232-253°C.

Preparation of 2:4-dinitrophenylhydrazone of 1-benzoyl-naphthalene.

There was no reaction with Allen's method. With Brady's method a solid separated after refluxing for 15 minutes. The mixture was cooled and the orange-red solid filtered, M.P. 245-247°C. This was crystallised from a mixture of glacial acetic acid and ethanol giving a crystalline solid, M.P. 248-249°C. with sintering from 230°C. This solid was much darker in colour than the 2:4-dinitrophenylhydrazone obtained from the 2-benzoyl-naphthalene.

This material was shown by mixed M.P. to be identical with a sample of 2:4-dinitrophenylhydrazone of 1-benzoyl-naphthalene prepared by Mr D. Robertson. Mr Robertson's sample was analysed as follows:-

$C_{23}H_{16}O_4N_4$ requires N, 13.6%.
found N, 13.8%.

Separation of mixture of benzoyl-naphthalenes.

The crude mixture of benzoyl-naphthalenes (15 g.) was chromatographed on a column of alumina (24.5" long x 1.18" diameter) with benzene as solvent. The solid was adsorbed at the top of the column as a dark band.

The/

The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°) when the dark band moved down the column. Fractions were collected as shown below and worked up in the usual way.

A. Forerunnings of the dark red band.

This gave an oil (0.12 g.). Nothing further was done with this.

B. The dark band which showed a heavy yellow fluorescence under the ultra-violet lamp.

This gave a dark oil (9.70 g.) which solidified gradually on standing for almost a week. The M.P. of the solid was very indefinite and over a wide range below 75°C. A little of this crude solid was crystallised from light petroleum (40-60°) giving clusters of needles. The crystallised solid was pressed on porous tile, M.P. 71-75°C. A mixed M.P. with pure 2-benzoyl-naphthalene gave a definite depression.

The 2:4-dinitrophenylhydrazone was formed on a little of this fraction. Brady's method was found to be necessary. The crude solid was crystallised from a mixture of alcohol and glacial acetic acid. The crystallised material had a M.P. 203-238°C., the residue M.P. 221-227°C. These melting-points indicated that the fraction was a mixture and not pure/

pure 1- or 2-benzoyl-naphthalene.

C. The column looked perfectly clear and had no colour, either visible or under the ultra-violet lamp. The eluate was deep yellow coloured and fluorescedce under the ultra-violet lamp. Development was continued until the eluate seemed free from yellow colour.

This gave a dark oil (2.92 g.) which tended to crystallise to a colourless solid. The M.P. of the solid was very indefinite below 70°C. The oily solid was crystallised from light petroleum (40-60°) and gave clusters of white needles, M.P. 75-80°C.

The 2:4-dinitrophenylhydrazone was prepared on this fraction and formed easily by Allen's method. The crude orange solid was crystallised from a mixture of alcohol and glacial acetic acid, M.P. 231-234°C. A mixed M.P. with the 2:4-dinitrophenylhydrazone of 2-benzoyl-naphthalene gave no depression, showing that this fraction was essentially the 2-compound.

D. Further eluate collected giving an almost colourless solution.

This gave 1.19 g. material which was very similar in appearance to fraction C. This was crystallised from light petroleum (40-60°) giving clusters of white needles, M.P. 76-82°C.

Some of the crude material was crystallised from aqueous alcohol and filtered from a trace of oily impurity, giving colourless needles, M.P. 80-82°C.

A/

A mixed M.P. with 2-benzoyl-naphthalene gave no depression. A mixed M.P. with 1-benzoyl-naphthalene gave a definite depression.

The 2:4-dinitrophenylhydrazone was prepared on this fraction and formed easily by Allen's method. The crude solid was crystallised from a mixture of alcohol and glacial acetic acid, M.P. 231.5-234°C. All the evidence showed that this fraction was essentially the 2-compound.

E. The column was drained by suction.

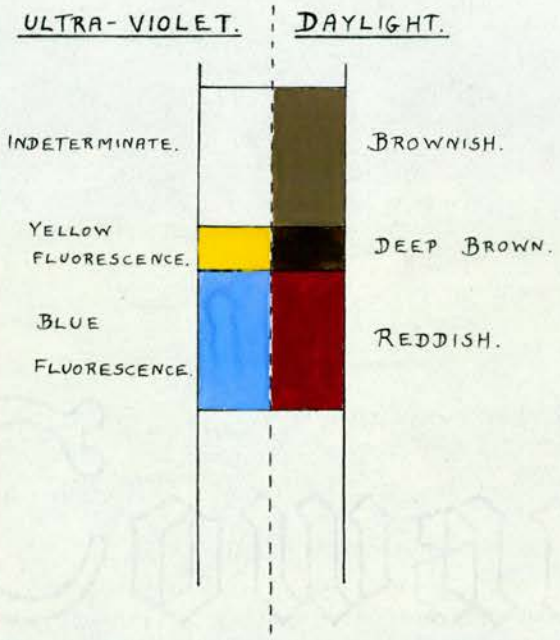
This gave 0.64 g. solid which was crystallised from light petroleum (40-60°) giving colourless needles, M.P. 79-82°C. The 2:4-dinitrophenyl-hydrazone was prepared on this fraction and formed easily by Allen's method. This was shown by M.P. and mixed M.P. to be the 2-compound.

Recovery from the column = 14.57 g. ≡ 97% Th.

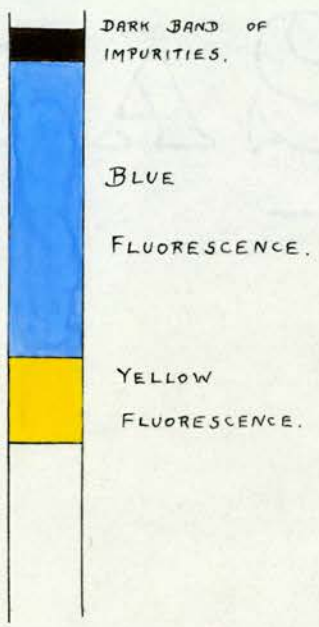
Conclusion: Chromatographic adsorption gave a partial separation of the crude mixture into an impure fraction and pure 2-benzoyl-naphthalene.

The material obtained from fraction B of the last chromatographic analysis (1 g.) was dissolved in benzene and rechromatographed on a column of alumina (20" long x 0.86" diameter). When all the/

the solid was adsorbed the column appeared as shown in the accompanying diagram. The column was developed with light petroleum (80-100°) when the red band broadened, became less intense in colour and was eluted giving a clean separation.



The column then appeared under the ultra-violet lamp as shown in the accompanying diagram. Development was continued with a 3:1 mixture of benzene and light petroleum (80-100°). This treatment eluted the yellow band, leaving the column uniformly blue under the ultra-violet lamp. The blue fluorescent material was eluted with benzene and 1% alcohol which left the column perfectly clear. Fractions were collected as shown below and worked up in the usual way.



A. /

A. Forerunnings of the red band.

This was blank.

B. The red band eluted with light petroleum (80-100°).

This gave a minute quantity of a red oil which was discarded.

C, D and E. Fractions of mixed solvent collected before the yellow band was eluted.

These were blank.

F. The main yellow band.

This gave an oily solid (0.17 g.) which was triturated with methyl alcohol to give a solid, M.P. 70-74°C. A mixed M.P. with pure 1-benzoyl-naphthalene gave no depression.

G. A cut between the yellow band and the blue fluorescence.

This gave an oily solid (0.20 g.) which was triturated with methyl alcohol to give a solid, M.P. 72-74°C. A mixed M.P. with pure 1-benzoyl-naphthalene gave no depression.

H. First fraction of benzene and 1% alcohol eluate.

This gave an oily solid (0.26 g.) which was triturated with methyl alcohol to give a solid, M.P. 74°C. which showed no depression in a mixed M.P. with 1-benzoyl-naphthalene.

I. Continued development with benzene and 1% alcohol until the column was absolutely clear.

This/

This gave an oily solid (0.29 g.) which was triturated with methyl alcohol. The resultant solid was crystallised from light petroleum (40-60°) giving colourless needles, M.P. 79-81°C. A mixed M.P. with pure 2-benzoyl-naphthalene gave no depression.

Recovery from the column = 0.92 g. ≡ 92% Th.

Conclusion: This column showed the possibility of separating a mixture of 1- and 2-benzoyl-naphthalene into the pure components.

Yield: The approximate yield ratio was calculated as follows:-

From the last chromatographic analysis

$$\text{Ratio of 2-benzoyl-naphthalene} = \frac{0.29}{0.92}$$

From the first chromatographic analysis

$$\text{Ratio of 2-benzoyl-naphthalene} = \frac{\frac{0.29 \times 9.70}{0.92} + 4.75}{14.57}$$

Therefore % 2-benzoyl-naphthalene in the total $= \frac{7.81 \times 100}{14.57} = 53.6\%$.

In a similar way,

% 1-benzoyl-naphthalene in the total = 46.4%.

Acetylation/

Acetylation of fluoranthene.

Buu—Hoï and Cagniant. Rec. Trav. Chim. 1943, 62,719.

Fluoranthene (20 g.) was dissolved in carbon disulphide (100 c.c.) and acetyl chloride (8 g.)added. The mixture was cooled in an ice/salt bath and powdered aluminium chloride (18 g.) added, with agitation, in small portions. The reactants were stirred at room temperature for 24 hours. The mixture was decomposed with ice-cold concentrated hydrochloric acid and the organic material extracted with ether. The ether extract was washed successively with water, sodium carbonate solution and finally with water until free from alkali. The ethereal solution was dried over anhydrous calcium chloride and the ether distilled off, yielding an orange oily solid (18 g.).

Attempt to separate acetyl-fluoranthenes by means of the picrates.

The picrate was formed on the crude solid (1 g.) as described in Campbell, p. 84, with benzene as solvent. M.P. of crude picrate 114-130°C. This was crystallised from methyl alcohol, M.P. 174-181°C. with sintering.

The picrate was decomposed by boiling with sodium hydroxide solution and extracting with ether. This gave a solid, M.P. 108-110°C. which gave no depression in a mixed M.P. with fluoranthene.

Attempt/

Attempt to separate the mixture by chromatography.

The crude solid (1.5 g.) was dissolved in cold benzene and chromatographed on a column of alumina (24.5" long x 0.86" diameter). The solid was adsorbed as a yellow band at the top of the column, with a blue fluorescence emerging from the bottom. Development with light petroleum (80-100°) gave a complete elution of the blue fluorescent material leaving the yellow band intact on the column. The column was next developed with benzene which caused the yellow band to descend the column very slowly, leaving a blue fluorescent material behind. The yellow band was eluted with 1% alcohol in benzene. The column was finally developed with 5% alcohol in benzene which eluted the blue fluorescent material from the column leaving only some dark coloured bands of impurity near the top. Fractions were collected as shown below and worked up in the usual way.

A. Blue fluorescent material eluted with light petroleum (80-100°).

This gave a white solid which fluoresced blue under the ultra-violet lamp (0.88 g.). This was proved to be fluoranthene by M.P. and mixed M.P.

B. /

B. Cut between the blue fluorescence and the yellow band.

This gave an oil of negligible weight which was triturated with methyl alcohol to give an oily solid, M.P. 70-105°C. This was discarded.

C. Main yellow band.

This gave a yellow solid (0.10 g.), M.P. 124-130°C. In an attempt to crystallise the solid, it was dissolved in methyl alcohol, ethyl alcohol and glacial acetic acid. Even so, there still remained a small insoluble residue which was filtered off. The solid was recovered by adding water to the mixed solvent, M.P. 124-127°C. This was recrystallised from methyl alcohol M.P. 128-129°C. This substance was analysed for acetyl-fluoranthene as follows:-

$C_{18}H_{12}O$ requires C, 88.53%; H, 4.92%.

found C, 88.16%; H, 4.75%.

D. Cut between the yellow band and the second blue fluorescence.

This gave a yellow solid (0.09 g.) which was crystallised from ethyl alcohol, M.P. 127-129°C.

E. First fraction of second blue fluorescence.

This gave a pale yellow solid (0.22 g.) which was crystallised from methyl alcohol giving fine plates, M.P. 101-102°C. This was analysed for acetyl/

acetyl-fluoranthene as follows:-

$C_{18}H_{12}O$ requires C, 88.53%; H, 4.92%.

found C, 87.44%; H, 4.70%.

F. Dark coloured bands from top of column.

This gave a very oily orange solid (0.10 g.). After prolonged trituration with methyl alcohol this turned solid, M.P. $<$ 70-90°C. An unsuccessful attempt was made to crystallise this solid from methyl alcohol. This fraction was not investigated further.

G. Final drainings of the column.

This gave a dirty oily orange solid (0.05 g.). An attempt was made to crystallise this substance from methyl alcohol but it turned to an oil and would not dissolve, so it was not investigated further.

Recovery from column = 1.44 g. ≡ 96% Th.

Conclusion: This column showed the presence of 60% unchanged fluoranthene in the mixture. Of the reacted material there were two main isomers in approximately equal quantities.

Attempt to separate the unchanged fluoranthene as the picrate and separate the rest of the mixture by chromatography.

It was assumed that 60% of the product was unchanged fluoranthene. The picrate was prepared from the crude mixture (16 g.) and picric acid (10 g.) in boiling/

boiling alcoholic solutions. The resultant picrate was decomposed by boiling with 10% sodium hydroxide solution and extracting with ether. This gave an almost colourless solid (7 g.), M.P. 107-110°C. which fluoresced blue under the ultra-violet lamp. A mixed M.P. with fluoranthene gave no depression.

The alcoholic filtrate from the solid picrate was diluted with 1500 c.c. water, made alkaline with caustic soda solution and boiled. Extraction of the aqueous solution with a mixture of ether and benzene and the usual treatment of the extract gave a yellow solid (3.8 g.). The ether separation of the sodium hydroxide solution was very difficult and resulted in an emulsion. Large volumes of benzene had to be added before the emulsion 'broke', but even then the separation was not very clean.

The yellow solid (3.8 g.) was chromatographed on a column of alumina (17" long x 1.38" diameter), with benzene as solvent. The solid was adsorbed as a broad yellow band with a blue fluorescence emerging from the bottom. Development was started with light petroleum (80-100°) which eluted the blue fluorescent material completely. The yellow band broadened, moved down the column and was partially eluted. Fractions/

Fractions were collected as shown below and worked up in the usual way.

A. Blue fluorescent material eluted with light petroleum (80-100°).

This gave a colourless solid (0.42 g.) which fluoresced blue under the ultra-violet lamp, M.P. 105-110°C. A mixed M.P. with fluoranthene gave no depression.

B. A cut between the blue fluorescence and the yellow band.

This gave a pale yellow solid (1.25 g.), M.P. 98-106°C. with sintering. This was crystallised from alcohol giving colourless crystals, M.P. 108-110°C. A mixed M.P. with fluoranthene gave no depression.

C. Main part of yellow band eluted with light petroleum (80-100°).

This gave a slightly yellow solid (0.24 g.), M.P. 85-96°C. This was crystallised from alcohol, M.P. 98-108°C., and was apparently a mixed fraction - possibly impure fluoranthene. The solid was not investigated further.

D. A further fraction of light petroleum (80-100°) eluate, very pale yellow.

This gave yellow needles (0.06 g.), M.P. <70-87°C., and was crystallised from alcohol, M.P.125-129°C.

After/

After this treatment the column appeared uniformly yellow in visible light and blue fluorescent under the ultra-violet lamp. The column was further developed with benzene when the visible yellow colour concentrated and moved to the bottom of the column. Further fractions were collected as shown below.

E. First fraction of benzene eluate.

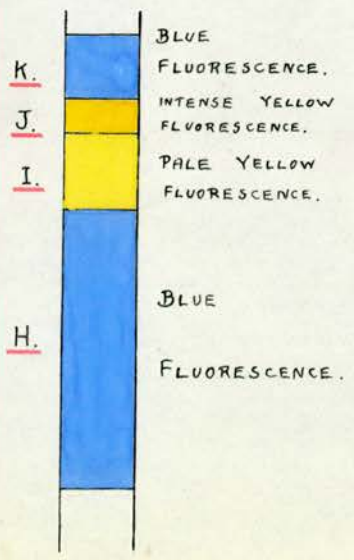
This gave yellow needles (0.03 g.), M.P. 122-129°C., and was crystallised from alcohol, M.P. 130-131°C.

F. Yellow material eluted with benzene.

This gave pale yellow clusters of needles (1.08 g.), M.P. 80-88°C., and was crystallised from alcohol, M.P. 90-101°C. A mixed M.P. with the low M.P. acetyl-fluoranthene obtained in the first trial purification was 82-97°C.

G. The column was drained and sucked dry.

This gave a solid crystallising in rhombic prisms (0.20 g.), and was crystallised from alcohol M.P. 101-103°C. The column then appeared under the ultra-violet lamp as shown in the accompanying diagram. The column of alumina was extruded, cut into sections as shown and each section extracted with boiling alcohol. The solid was recovered from each section by distillation/



distillation and evaporation.

H. The blue fluorescence at the bottom of the column.

This gave an oily scum of negligible weight and was not investigated further.

I. Pale yellow colour on the column extracted with alcohol.

This gave a yellow solid (0.03 g.) which was crystallised from alcohol, M.P. 136-140°C.

J. The intense yellow band left on the column.

This gave a slightly oily solid (0.30 g.), and was crystallised from alcohol leaving a residue. The M.P. of the crystallised material was 135-139°C. A mixed M.P. with the high M.P. isomer acetyl-fluoranthene gave a depression, 104-125°C. The crystallised solid was recrystallised from a mixture of alcohol and glacial acetic acid giving yellow needles, M.P. 138-141°C.

The residue was crystallised from a mixture of alcohol and glacial acetic acid giving yellow needles, M.P. 140-142°C. This substance was analysed as a possible diacetyl-fluoranthene as follows:-

$C_{20}H_{14}O_2$ requires C, 83.9%; H, 4.89%.

found C, 82.6%; H, 5.25%.

K. The blue fluorescence at the top of the column.

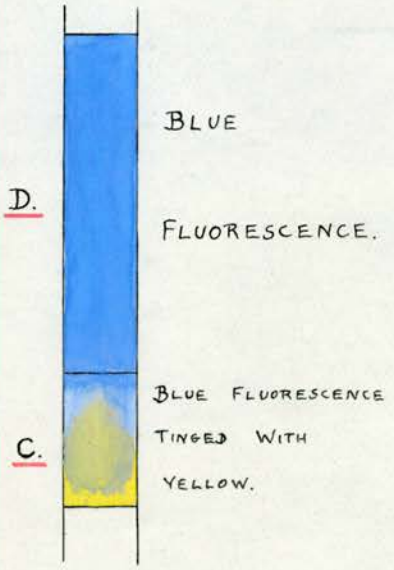
This gave a dark orange-red oil (0.10 g.) which did not solidify even after prolonged trituration with methyl/

methyl alcohol, and was not investigated further.

Recovery from column = 3.71 g. ≡ 97.6%.Th.

Conclusion: The column gave a partial separation of the crude mixture into fluoranthene, an impure acetyl-fluoranthene, the low M.P. acetyl-fluoranthene and a diacetyl-fluoranthene.

The material from fraction F (0.95 g.) of the above chromatographic analysis was rechromatographed on a column of alumina (11.5" long x 0.63" diameter) with benzene as solvent. The material was adsorbed as a visible yellow band having a yellow fluorescence under the ultra-violet lamp. The column was developed with light petroleum (80-100°) and the yellow band eluted by this treatment. The column was drained and appeared under the ultra-violet lamp as shown in the accompanying diagram. The alumina was extruded, cut into sections as shown and each section extracted with boiling alcohol. The various fractions were collected as shown below and worked up in the usual way.



A. Main yellow band.

This gave a yellow solid (0.62 g.) which was crystallised/

crystallised from alcohol, M.P. 110-126°C., and on recrystallisation from alcohol gave yellow needles, M.P. 123-128°C. The mother liquor from the first crystallisation gave a further crop of crystals on standing, M.P. 78-96°C. This substance was not investigated further.

B. Drainings of the column.

This gave a yellow solid (0.10 g.) which was crystallised from alcohol, M.P. 81-94°C. This was not investigated further.

C. The bottom of the column extracted with alcohol.

This gave a pale yellow solid (0.11 g.) which was crystallised from alcohol, M.P. 94-100°C.

D. The top part of the column extracted with alcohol.

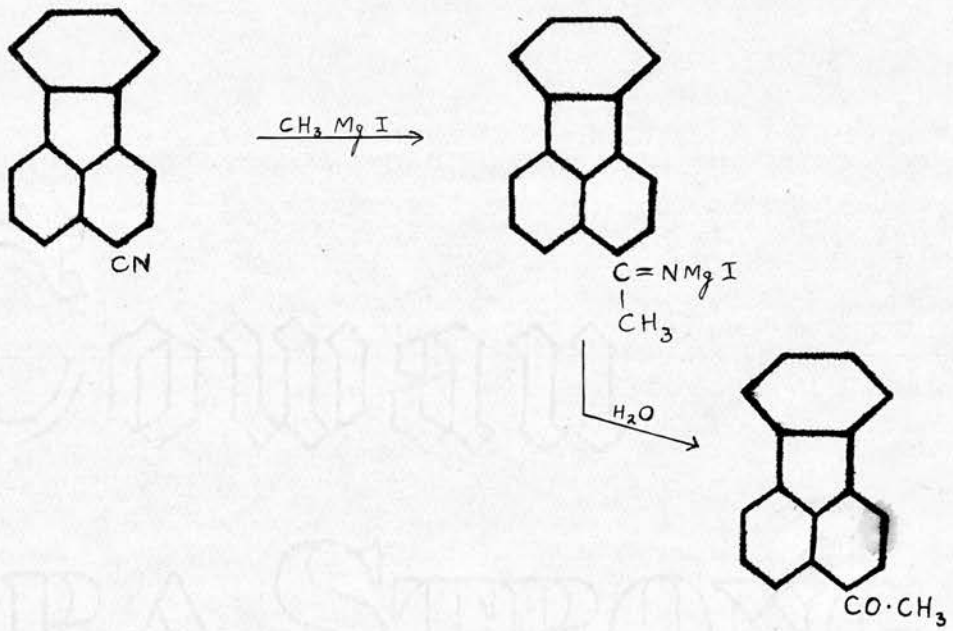
This gave an oily yellow solid (0.07 g.). An attempt was made to crystallise this material from alcohol but the physical state of the solid could not be improved in this way.

Recovery from column = 0.90 g. ≡ 94.7% Th.

Conclusion: This column gave a further separation of the mixed fraction into the two component isomers although the separation was not absolute.

Preparation /

Preparation of 4-acetyl-fluoranthene from 4-cyano-fluoranthene.



Methyl-magnesium iodide was prepared from magnesium turnings (0.10 g.) and methyl iodide (0.60 g.) in anhydrous ether (2 c.c.). 4-Cyano-fluoranthene (0.15 g.) in anhydrous benzene (25 c.c.) was added, when a solid immediately precipitated. The mixture was refluxed for 40 hours leaving a deeply fluorescent solution. This solution was decomposed with dilute sulphuric acid, steam distilled and the oily-aqueous mixture extracted with a mixture of ether and benzene. The resulting dark brown solution was dried over anhydrous calcium chloride.

This solution was chromatographed on a column of alumina (5.5" long x 0.53" diameter) when the substance/

substance was adsorbed as a dark band at the top of the column. The column was developed with 1% alcohol in benzene when a yellow band moved down the column and was eluted leaving a dirty brown band at the top.

The solvent was evaporated leaving a dirty yellow oily solid which was triturated with methyl alcohol. The resultant solid was crystallised from ethyl alcohol and carbon screened leaving an oily residue. A very small amount of dirty yellow solid crystallised, M.P. $<$80-110°C. The filtrate was reduced to about one third of its bulk when a pale yellow solid separated on standing, M.P. 122-128°C. with sintering.

This solid was dissolved in benzene and re-chromatographed on a column of alumina (8" long x 0.53" diameter). The solid was adsorbed as a yellow band. The column was developed with benzene when a blue fluorescence emerged from the yellow band and was eluted completely. The visible yellow band, showing a bright yellowish green fluorescence under the ultra-violet lamp, was eluted with benzene as a separate fraction leaving the column with a slight blue fluorescence.

The yellow coloured fraction gave a deep yellow solid which was crystallised from alcohol giving clusters/

clusters of yellow needles, M.P. 131-132°C. This solid was separated, pressed on porous tile and recrystallised from alcohol, M.P. 131-132°C. A mixed M.P. with 4-cyano-fluoranthene gave a definite depression, <90-100°C.

A mixed M.P. with the high M.P. isomer obtained from the crude mixture in the Friedel-Crafts reaction gave no depression showing that this material was indeed 4-acetyl-fluoranthene.

A mixed M.P. with the low M.P. isomer obtained from the crude mixture in the Friedel-Crafts reaction gave a definite depression indicating that this material was 11-acetyl-fluoranthene.

Derivatives of 4-acetyl-fluoranthene.

2:4-dinitrophenylhydrazone.

This was formed easily by Allen's method. An attempt was made to crystallise the crude material from a mixture of alcohol and glacial acetic acid. The solid was very insoluble but assumed a cleaner and brighter appearance after boiling in the mixed solvent for some time. The residue, M.P. 261-262°C. after some sublimation from 250°C., was analysed for the 2:4-dinitrophenylhydrazone of 4-acetyl-fluoranthene as follows:-

$C_{24}H_{16}O_4N_4$ requires N, 13.20%.

found N, 14.30%.

Oxime/

Oxime

4-Acetyl-fluoranthene (0.06 g.) was refluxed in pyridine (2.4 c.c.) with hydroxylamine hydrochloride (0.24 g.) for 7 hours. Globules of yellow oil, which had formed, solidified on cooling. The mixture was triturated with water, and the filtered solid crystallised from alcohol. A crystalline solid formed on standing, M.P. 195.5-198°C. This was analysed for the oxime of 4-acetyl-fluoranthene as follows:-

$C_{18}H_{13}ON$ requires N, 5.41%.

found N, 4.67%.

Attempted Beckmann rearrangement on oxime.

The oxime of 4-acetyl-fluoranthene (0.02 g.) was mixed with phosphorus pentachloride (0.10 g.) in anhydrous ether (10 c.c.) and allowed to stand with frequent shaking for 3 days. The ether was distilled off leaving a dark oil which was triturated with water to a brown oily solid. This was dissolved in light petroleum (80-100°), filtered from a dark residue and the resultant yellow solution left to crystallise slowly, yielding a light grey solid, M.P. 182-189°C. A mixed M.P. with the parent oxime gave a definite depression (170-177°C), indicating that the Beckmann reaction had occurred. Owing to the small amount of material/

material available nothing further was done with it.

Derivatives of 11-acetyl-fluoranthene.

2:4-dinitrophenylhydrazone.

This was formed as detailed above for the 4-isomer. The crude solid was boiled with a mixture of alcohol and glacial acetic acid. The residue sublimed giving orange needles, M.P. 299-301°C. This material was analysed for the 2:4-dinitrophenylhydrazone of 11-acetyl-fluoranthene as follows:-

$C_{24}H_{16}O_4N_4$ requires N, 13.20%.

found N, 12.50%.

Oxime.

This was formed as detailed above for the 4-isomer using 11-acetyl-fluoranthene (0.10 g.), hydroxylamine hydrochloride (0.40 g.) and pyridine (4 c.c.). The crude solid was crystallised from glacial acetic acid plus a little alcohol giving a solid, M.P. 173-178°C. with some sublimation. This was analysed for the oxime of 11-acetyl-fluoranthene as follows:-

$C_{18}H_{13}ON$ requires N, 5.41%.

found N, 5.56%.

Attempted Beckmann rearrangement on oxime.

This was done as detailed for the 4-isomer, using the oxime of 11-acetyl-fluoranthene (0.04 g.), phosphorus/

phosphorus pentachloride (0.10 g.) and anhydrous ether (20 c.c.). The crude solid was chromatographed on a column of alumina (3.5" long x 0.4" diameter) using benzene as solvent when the solid was adsorbed as a dark brown band. The column was developed with benzene when a yellow band moved down the column and was eluted, leaving the column blank except for dark brown impurities at the top.

The solvent was distilled off from the yellow fraction, leaving a brown oil which was triturated with methyl alcohol until solid. This was dissolved in light petroleum (80-100°), filtered from a dirty residue and left to crystallise slowly. This gave a dark solid of rather indefinite M.P., 117-122°C. with signs of darkening. A mixed M.P. with the parent oxime was very indefinite and inconclusive. Nothing further was done with the product.

Benzoylation of tetrahydrofluoranthene by the Perrier modification of the Friedel-Crafts reaction.

Fieser's 'Experiments in Organic Chemistry', p.192.

The Perrier addition product was prepared from benzoyl chloride (8 g.) and powdered aluminium chloride (8 g.) and dissolved in carbon disulphide (60 c.c.). Tetrahydrofluoranthene (11 g.) was added slowly and there was a fairly brisk evolution of hydrochloric acid gas. The completed reaction mixture was decomposed/

decomposed and worked up as detailed on p.32 to give a crude yellow solid.

Yield = 11 g. ≡ 66.6% Th.

The crude solid was dissolved in benzene and chromatographed on a column of alumina (20" long x 1.38" diameter). The solid was adsorbed as a visible yellow band (5" long) with a blue fluorescence below (c. 1" long). The column was developed with light petroleum (80-100°) when the yellow band broadened and moved down the column until it appeared uniformly yellow in visible light and greenish yellow under the ultra-violet lamp. There was no sign of bands separating. The column was subsequently developed with a 3:1 mixture of benzene and light petroleum (80-100°); benzene; benzene and 1% alcohol; and finally benzene and 5% alcohol. Fractions were collected from the various development liquors as indicated below. Each fraction was worked up in the usual way.

A. Development with light petroleum (80-100°). The blue fluorescent material was eluted and collected until the eluate was tinged with yellow although the column was still blue coloured at the bottom.

This gave a yellow oily solid (0.58 g.) which had a blue fluorescence. Attempts were made to crystallise this solid from alcohol and light petroleum/

petroleum (80-100°) but it persisted in coming down as an oil.

B. Benzene/light petroleum fraction. Yellow material containing a little blue fluorescent material from the bottom of the column.

This gave a dark yellow oily solid (1.15 g.) with a little blue fluorescent material admixed. The solid would not solidify completely, even on prolonged trituration with methyl alcohol. The oily solid was crystallised from alcohol and gave a bright yellow solution and a trace of a yellow insoluble residue. A yellow crystalline solid separated from the alcoholic solution. This solid was almost colourless when crushed on porous tile, M.P. 132-138°C.

C. Benzene/light petroleum fraction. When the yellow substance was completely eluted the column was a dirty blue colour when viewed under the ultra-violet lamp and pale yellow in visible light. Development was continued with 250 c.c. mixed solvent.

This gave a white crystalline material (0.27 g.) in a yellow solution. The solid was crystallised from alcohol and gave pale yellow prisms which were almost colourless when pressed on porous tile, M.P. 142-143°C. This substance was analysed for 4-benzoyl-tetra/

tetrahydrofluoranthene as follows:-

$C_{23}H_{18}O$ requires C, 89.02%; H, 5.81%.

found C, 88.39%; H, 5.75%.

The benzoyl-tetrahydrofluoranthene was not very soluble in alcohol and left a small residue, M.P. 142-143°C.

D. Development was changed to benzene and the eluate collected until it started showing a yellow tinge again.

This gave white crystals in a yellow solution (0.79 g.). This solid was crystallised from alcohol, leaving a small residue, M.P. 141-143°C., and gave pale yellow prisms, M.P. 141-143°C. This solid was recrystallised from glacial acetic acid and gave almost colourless prisms, M.P. 144.5-145.5°C., which fluoresced blue under the ultra-violet lamp.

E. Yellow coloured benzene eluate.

This gave a mass of white crystals in a yellow solution (4.05 g.). This solid was crystallised from alcohol, leaving a small residue, M.P. 143-145°C., and was deposited as a mixture of white and pale yellow crystals. An attempt was made to hand-pick some of the crystals and determine the M.P. of each species but the results were inconclusive.

White crystal - M.P. 105-112°C.
Yellow crystal - M.P. 100-130°C.

F./

F. Benzene eluate collected until very pale yellow.

This gave a dark yellow solid (0.91 g.) which was crystallised from glacial acetic acid and gave pale yellow crystals which were almost white when crushed, M.P. 139-141°C. A mixed M.P. with the substance obtained from fraction D gave no depression.

G. Benzene and 1% alcohol fraction. The eluate was very pale yellow in colour.

This gave an oily orange solid (0. 38 g.) which was crystallised from glacial acetic acid and gave a small amount of pale yellow crystals, M.P. 138-140°C.

H. Benzene and 5% alcohol fraction. The eluate was pale yellow in colour.

This gave an orange solid (0. 13 g.). An attempt was made to crystallise this from glacial acetic acid but nothing was obtained.

I. Benzene and 5% alcohol fraction.

This fraction was similar in appearance to fraction H and was treated in the same way to give an oily solid (0.15 g.) which did not crystallise from glacial acetic acid.

J. Benzene and 5% alcohol fraction. An orange yellow band moved down the column with this development. This fraction was a cut at the beginning of this band.

This gave an orange resin (0.79 g.). Attempted crystallisation from a mixture of alcohol and glacial acetic acid gave only an oil.

K./

K. Benzene and 5% alcohol fraction. The orange yellow band was collected separately.

This gave an orange resinous solid (0.98 g.) which came down as an oil when a solution in a mixture of alcohol and glacial acetic acid was cooled.

L. The column was washed through with alcohol.

This gave an oily orange solid (0.08 g.) which was discarded after an unsuccessful attempt to crystallise it from alcohol.

Recovery from the column = 10.26 g. = 93.3% Th.

Conclusion: This chromatographic analysis showed the presence of one pure benzoyl-tetrahydrofluoranthene in bulk and the possible presence of another (fraction E). These were separated from some dark orange resinous solid.

Fractions A and B from the above chromatographic analysis were combined again, the alcohol was evaporated completely from the mother liquors, and the whole (1.52 g.) was rechromatographed on a column of alumina (18" long x 0.86" diameter) with benzene as solvent. The substance was adsorbed as a dark yellow band with a blue fluorescent material emerging from it. The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°) when the blue fluorescent material was completely eluted, leaving the column uniformly yellow. The column was subsequently/

sequently developed with benzene and 2% alcohol. Fractions were collected as shown below and each was worked up in the usual way.

A. The blue fluorescent material eluted with the benzene/light petroleum mixture.

This gave an almost white oily solid (0.46 g.) with a blue fluorescence. This was crystallised from alcohol which left a small yellow oily residue which would not solidify even on prolonged trituration with methyl alcohol. The alcoholic solution was allowed to evaporate slowly and gave a white solid, M.P. 64-69°C. which was proved by mixed M.P. to be impure tetrahydrofluoranthene.

B. Continued development with mixed solvent gave a yellow eluate.

This gave a yellow solid (0.26 g.) which was crystallised from alcohol and gave yellow crystals, M.P. 132-140°C. This was proved by mixed M.P. to be impure benzoyl-tetrahydrofluoranthene, the same as was analysed in the first chromatographic analysis.

C. Fraction of 100 c.c. benzene and 2% alcohol.

This gave a pale yellow solid (0.42 g.) which was crystallised from alcohol and gave an almost white solid, M.P. 143-144°C.

D. A fraction similar to C.

This gave a yellow resinous solid (0.12 g.).

E. /

E. A fraction similar to C.

This gave a yellow oily solid (0.05 g.). Fractions D and E were crystallised together from alcohol and gave a yellow solid which was colourless when pressed on porous tile, M.P. 143-145°C.

Recovery from the column = 1.31 g. ≡ 86.2% Th.

Conclusion: This chromatographic analysis showed that fractions A and B from the original column were a mixture of tetrahydrofluoranthene and benzoyl-tetrahydrofluoranthene and gave a good separation of the mixture into its components.

The crystallised solid from fraction E of the original chromatographic analysis (2.40 g.), see p.133, was dissolved in benzene and rechromatographed on a column of alumina (15.5" long x 0.86" diameter). The substance was adsorbed quite uniformly on the column and no distinctive bands could be seen, either in visible or ultra-violet light. Three fractions of eluate, each of 100 c.c. of a 3:1 mixture of benzene and light petroleum (80-100°), were collected, followed by two fractions each of 100 c.c. benzene. The various fractions were worked up in the usual way.

A. This gave an almost white solid (1.15 g.), M.P. 100-130°C. This was crystallised from alcohol leaving a/

a residue, M.P. 143-144°C. The alcoholic solution deposited a first crop of crystals, M.P. 138-142°C. which was proved by mixed M.P. to be the same benzoyltetrahydrofluoranthene as was analysed. A second small crop of crystals which were deposited on standing had a M.P. 95-120°C. Nothing further was done on this material. The residue was crystallised from alcohol, M.P. 144-145°C.

B. This gave an almost white solid (0.68 g.), M.P. 100-125°C. which was crystallised from alcohol leaving a very small residue, M.P. 139-141°C. The crystallised material separated as a mixture of glistening plates and clusters of needles, the latter in bulk. The M.P. of the conglomerate mass was 100-132°C. A crystal of the plate material was hand-picked and gave quite a sharp M.P., 118-122°C. A little of the mixture was recrystallised from glacial acetic acid and gave clusters of white needles, M.P. 143-145°C.

An attempt was made to characterise this fraction by preparing the 2:4-dinitrophenylhydrazone by Allen's method but was unsuccessful.

C. This gave a white solid (0.37 g.) which crystallised from alcohol in clusters of needles, M.P. 143-146°C.

D. This gave a pale yellow solid (0.15 g.) which was crystallised from alcohol, M.P. 139-143°C.

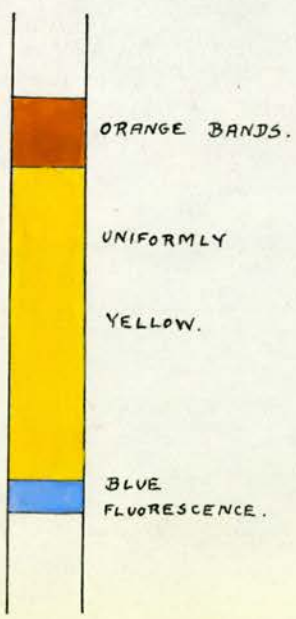
E. /

E. This gave an orange oil (0.07 g.), but an attempt to crystallise it from alcohol gave only an oil. Nothing further was done with this material.

Recovery from the column = 2.42 g. ≡ 100% Th.

Conclusion: This chromatographic analysis showed that fraction E of the original column was essentially the same benzoyl-tetrahydrofluoranthene which had been analysed. It also showed the presence of a trace of a second substance, M.P. 118-122°C.

In a further search for the second substance spotted in the last chromatographic analysis, the mother liquors from the crystallisations of fractions E, F and G, together with the remaining fractions from the original column (pp. 133-135) were combined and the solvent evaporated. This gave a dark orange oil (3.56 g.), which was dissolved in benzene and rechromatographed on a column of alumina (22" long x 0.86" diameter). When the substance was all adsorbed, the column appeared to have a series of orange bands about 3" from the top of the column, the remainder of which was a nondescript yellow colour. Under the ultra-violet lamp a little blue fluorescent material was seen to be emerging from the yellow substance (see accompanying diagram). The column/



column was developed with benzene until free from yellow colour. The orange bands were subsequently eluted with alcohol. Fractions were collected as shown below and worked up in the usual way.

A. Benzene eluate collected until it just started to show yellow.

This fraction was blank.

B. A 'blind' fraction of 100 c.c. benzene.

This gave a yellow resinous solid (0.40 g.) which gave a yellow solid, M.P. 86-97°C., on trituration with alcohol. An attempt was made to crystallise this solid from alcohol but it came down oily. The oil was redissolved in ether and the mixed solvent left so that the ether would evaporate slowly. This gave a white crystalline solid, M.P. 100-114°C.

C. A 'blind' fraction of 100 c.c. benzene.

This gave a yellow resinous solid (0.72 g.) which was triturated with alcohol to give a solid, M.P. 70-85°C. Attempts were made to crystallise the solid from glacial acetic acid; light petroleum (80-100°); and chloroform, but the solid was very soluble in all of these solvents. Finally, the solid was dissolved in a mixture of alcohol and ether and left until the ether had evaporated. The solid still came down in an oily form.

The solid from fractions B and C was recrystallised

from/

from a mixture of alcohol and glacial acetic acid. This gave a yellow solid which was almost colourless when crushed on porous tile, M.P. 100-112°C. Nothing further was done with this.

D. A 'blind' fraction of 100 c.c. benzene.

This gave a yellow resinous solid (0.20 g.) which would not solidify even on prolonged trituration with alcohol. An attempt was made to crystallise the oily solid from alcohol but no improvement resulted.

The 2:4-dinitrophenylhydrazone was prepared from this oily solid. No reaction occurred with Allen's method. Brady's method was therefore tried and the mixture of oil (0.20 g.) and 2:4-dinitrophenylhydrazine (0.13 g.) refluxed together in alcohol (15 c.c.) and a few drops of concentrated sulphuric acid for twelve hours. An orange precipitate was obtained on adding dilute sulphuric acid. This was crystallised from a mixture of alcohol and glacial acetic acid and the solid reprecipitated by adding the minimum amount of water. A M.P. showed sintering at 190°C. and gradual charring from 280°C. upwards although the substance did not melt below 350°C. A mixed M.P. with 2:4-dinitrophenylhydrazine gave a depression, 191-205°C.

This substance was analysed for the 2:4-dinitrophenyl/

phenylhydrazone of benzoyl-tetrahydrofluoranthene as follows:-

$C_{29}H_{22}O_4N_4$ requires N, 11.43%.

found N, 11.40%.

E. A 'blind' fraction of 100 c.c. benzene.

This gave 0.22 g. yellow oily solid. Nothing further was done with this.

F. Alcoholic eluate - the fore-runnings of the orange band.

This gave 0.10 g. yellow oily solid.

G. The orange band and the drainings of the column.

This gave 1.40 g. orange resinous solid of indefinite M.P. No attempt was made to purify this further.

Recovery from the column = 3.04 g. = 85.4% Th.

Conclusion: The separation of the crude oil into its components was not absolute but this chromatographic analysis showed the possible presence of an impure isomeric benzoyl-tetrahydrofluoranthene characterised by its 2:4-dinitrophenylhydrazone.

Dehydrogenation of the residues from the last chromatographic analysis.

The residues from fractions B and C crystallised, E and F (0.99 g. in all) were refluxed for 24 hours with chloranil (1.60 g.) in boiling sulphur-free xylene (20 c.c.). The residue was very dark and tarry/

tarry at the end of the refluxing period. The xylene was diluted with an equal volume of ether, the tetrachlorohydroquinone extracted with 10% sodium hydroxide solution, and the ether/xylene mixture washed and dried. The solvent was distilled off.

The resultant orange oil was dissolved in benzene and chromatographed on a column of alumina (14" long x 0.86" diameter). The solid was adsorbed as a yellow band, 6.5" long, with dark coloured impurities at the top and a blue fluorescence emerging from the bottom. The column was developed with a 3:1 mixture of benzene and light petroleum (80-100°). Fractions were collected as shown below and worked up in the usual way.

A. Blue fluorescent eluate collected until it was tinged with yellow.

This gave a yellow oily solid (0.06 g.). An attempt was made to crystallise this from alcohol but it persisted in coming down oily.

B. A cut between the blue fluorescent material and the visible yellow band.

This gave a yellow oily solid (0.07 g.), and on treatment as fraction A gave a similar result.

C. The main yellow band.

This gave a yellow resinous solid (0.20 g.). This was treated as fraction A but persisted in coming/

coming down oily.

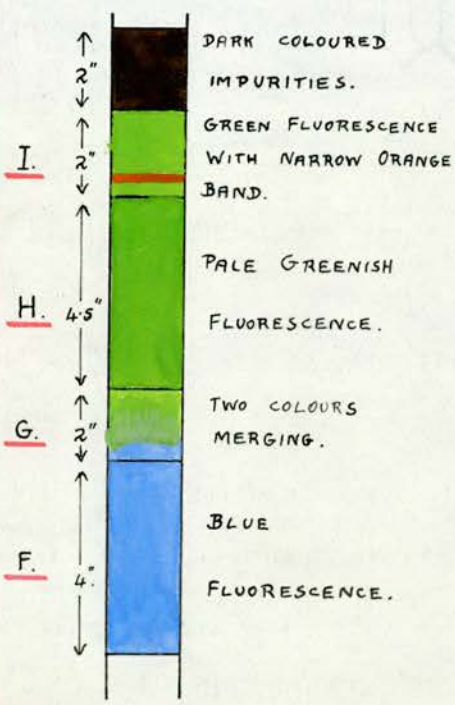
D. The last of the yellow band.

This gave a yellow oily solid (0.07 g.) which did not solidify on prolonged trituration with alcohol. An attempt to crystallise the material from alcohol returned an oil.

Nothing further was done with these fractions.

E. The column was developed with 300 c.c. benzene and drained. The eluate was still yellow.

This gave a yellow resin (0.10 g.) which did not solidify on trituration with alcohol. This material was crystallised from alcohol and gave a yellow crystalline solid, M.P. 122-126°C. A mixed M.P. with 4-benzoyl-fluoranthene gave no depression.



The column then appeared under the ultra-violet lamp as shown in the accompanying diagram. The column was cut as shown and the various sections treated in the usual way.

F./

F. Blue fluorescence left at the bottom of the column. This gave a yellow solid (0.02 g.) which was crystallised from alcohol and gave a small amount of yellow solid, M.P. 125-129°C.

G. This gave 0.02 g. yellow solid which was crystallised from alcohol and gave a dark yellow crystalline solid, M.P. 173-178°C.

H. This gave 0.08 g. yellow solid which was crystallised from alcohol, in which it was not very soluble, and gave a dark yellow crystalline solid, M.P. 173-178°C.

This material was analysed for a possible dibenzoyl-fluoranthene as follows:-

$C_{30}H_{18}O_2$ requires C, 87.80%; H, 4.39%.
found C, 87.06%; H, 4.80%.

I. This gave 0.04 g. of a slightly orange solid. This was crystallised from alcohol and gave an orange yellow solid, M.P. 169-179°C. A little orange oily residue was filtered off during the crystallisation.

Recovery from the column = 0.66 g. ≡ 66% Th. from the starting material.

Conclusion: Chloranil dehydrogenation of the oily residues, followed by chromatographic analysis, showed the presence of 4-benzoyl-fluoranthene together with a dibenzoyl-fluoranthene, M.P. 173-178°C. The presence of a dibenzoyl-tetrahydrofluoranthene in the original/

original mixture was therefore demonstrated although it was not found possible to isolate this as such.

A quantitative survey of the successive chromatographic analyses carried out on the crude benzoyl-tetrahydrofluoranthene showed that the substance, M.P. 142-143°C., was present to the extent of at least 60% of the total. The dibenzoyl-tetrahydrofluoranthene was present in relatively small amount together with a second isomeric monobenzoyl-tetrahydrofluoranthene which was characterised by its 2:4-dinitrophenyl-hydrazone but was not isolated.

Dehydrogenation of Benzoyl-tetrahydrofluoranthene.

Benzoyl-tetrahydrofluoranthene, M.P. 143-145°C., (1 g.) was refluxed with chloranil (1.6 g.) in sulphur-free xylene (20 c.c.) for 24 hours. The xylene was diluted with an equal volume of ether and the tetra-chlorohydroquinone extracted with dilute sodium hydroxide solution. The xylene/ether solution was washed free from alkali and dried over anhydrous calcium chloride. When the solvent was evaporated off, a yellow solid separated, M.P. 123-126°C.

This solid was purified by chromatographing on a column of alumina (10.5" long x 0.86" diameter) with benzene as solvent. The solid was adsorbed as a yellow band, 3.5" long, with a slight blue fluorescence emerging from the bottom. Development of the column with/

with a 3:1 mixture of benzene and light petroleum (80-100°) gave a yellow eluate which deposited a yellow crystalline solid (0.65 g.). This was crystallised from alcohol and gave brilliant yellow needles, M.P. 131-132°C. A mixed M.P. with 11-benzoylfluoranthene gave a definite depression below 100°C. A mixed M.P. with 4-benzoylfluoranthene gave no depression which proved that the benzoyl-tetrahydrofluoranthene used in this dehydrogenation was the 4-benzoyl-5:6:7:8-tetrahydrofluoranthene.

Yield = 65% Th.

Derivatives of 4-benzoyl-tetrahydrofluoranthene.

Picrate:-

An attempt was made to prepare the picrate from boiling alcoholic solutions(Campbell, p. 84). This was unsuccessful and unchanged 4-benzoyl-tetrahydrofluoranthene was recovered (M.P. and mixed M.P.).

2:4-Dinitrophenylhydrazone.

An attempt to prepare this by Allen's method (Campbell, p. 87) was not successful.

The derivative was ultimately prepared by Brady's method from the ketone (0.15 g.) and solid 2:4-dinitrophenylhydrazine (0.10 g.) in boiling alcohol with a few drops of concentrated sulphuric acid. The mixture/

mixture was refluxed overnight and gave a dirty oily mass. A spot M.P. showed the presence only of impure 2:4-dinitrophenylhydrazine. Glacial acetic acid was added until the oil was in solution and refluxing continued for 3 hours longer. The reaction mixture gave with dilute sulphuric acid a crude solid which was crystallised from a mixture of glacial acetic acid and alcohol. Water was added to bring down an orange solid, M.P. 216-217°C. A mixed M.P. with 2:4-dinitrophenylhydrazine gave a definite depression, 177-195°C.

Analysis:

$C_{29}H_{22}O_4N_4$ requires N, 11.43%.
found N, 10.0%.

Oxidation of tetrahydrofluoranthene.

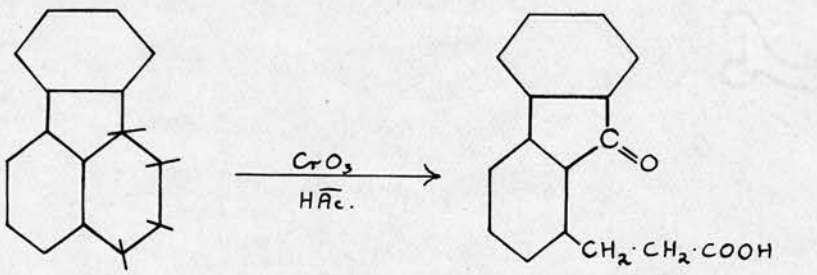
Kruber, Ber., 1931, 64, 84.

Fieser and Seligman, J.A.C.S., 1935, 57, 2175.

A solution of chromic anhydride (A.R., 4.70 g.) in water (4 c.c.) and glacial acetic acid (3 c.c.) was added slowly to a solution of tetrahydrofluoranthene (1.1 g.) in glacial acetic acid (27.5 c.c.), kept just below the boiling-point. The mixture was allowed to stand overnight when it was heated to boiling and refluxed for 1 hour. The solution was cooled, diluted into water (150 c.c.) and extracted with benzene. The yellow benzene extract was shaken with 10% sodium hydroxide/

hydroxide solution to extract any organic acid. The crude acid was precipitated with dilute hydrochloric acid and filtered. Purification was effected by boiling the crude acid with an aqueous suspension of barium carbonate and filtering off the excess. The barium salt solution was decomposed with dilute hydrochloric acid, the purified acid filtered and washed free from mineral acid. This gave an orange solid, M.P. 127-133°C. which was crystallised from glacial acetic acid. M.P. 130-132°C. (fluorenone-8-β-propionic acid, M.P. 137-138°C.).

Equation for the reaction.



·FLUORENONE-8-β-PROPIONIC ACID.

Oxidation/

Oxidation of fluoranthene.

Fieser and Seligman, J.A.C.S., 1935, 57, 2175.

A solution of chromic anhydride (A.R., 3.40 g.) in water (3 c.c.) and glacial acetic acid (2 c.c.) was added to a solution of fluoranthene (1 g.) in glacial acetic acid (25 c.c.). The reaction was carried through and worked up as detailed above for tetrahydrofluoranthene. The crude acid, M.P. 191-193°C. with sublimation to give orange prisms, was purified by boiling with an aqueous barium carbonate suspension. The barium salt was decomposed with hydrochloric acid and the organic acid extracted with benzene. The benzene extract was washed free from mineral acid and dried over anhydrous calcium chloride. The bulk of the benzene was distilled off and the acid left to crystallise, giving an orange solid, M.P. 196-197°C. This was analysed for fluorenone-1-carboxylic acid as follows:-

Calc. for $C_{14}H_8O_3$ C, 75.01%; H, 3.57%.

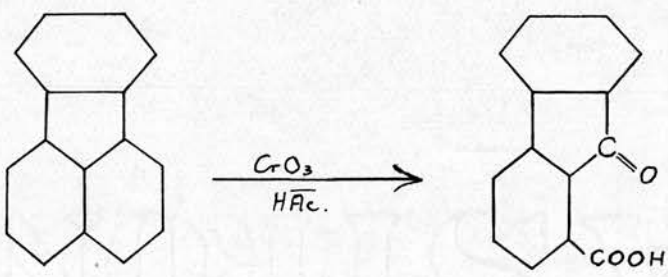
found C, 73.91%; H, 3.73%.

A little of the fluorenone-1-carboxylic acid prepared by Gerty (Thesis, Edinburgh, 1939, p. 54), M.P. 188°C. was crystallised from benzene and filtered from a small residue. The M.P. of the crystallised acid was 195-196°C. A mixed M.P. of the two acids gave/

gave no depression.

Yield = 0.48 g. ≡ 43.5% Th.

Equation for the reaction.



FLUORENONE-1-CARBOXYLIC ACID.

Oxidation of 4-benzoyl-fluoranthene.

A solution of chromic anhydride (A.R., 1.40 g.) in water (1 c.c.) and glacial acetic acid (1 c.c.) was slowly added to a solution of 4-benzoyl-fluoranthene (0.60 g.) in glacial acetic acid (10 c.c.). The mixture was allowed to stand overnight, raised to the boiling-point and refluxed for 2 hours. The mixture was worked up exactly as detailed above for the oxidation of fluoranthene, and gave a yellow solid, M.P. 227-228°C. This was analysed for 2-benzoyl-fluorenone-1-carboxylic acid as follows:-

$C_{21}H_{12}O_4$	requires	C, 76.83%;	H, 3.66%.
	found	C, 74.64%;	H, 3.57%.

Yield = 0.18 g. ≡ 28% Th.

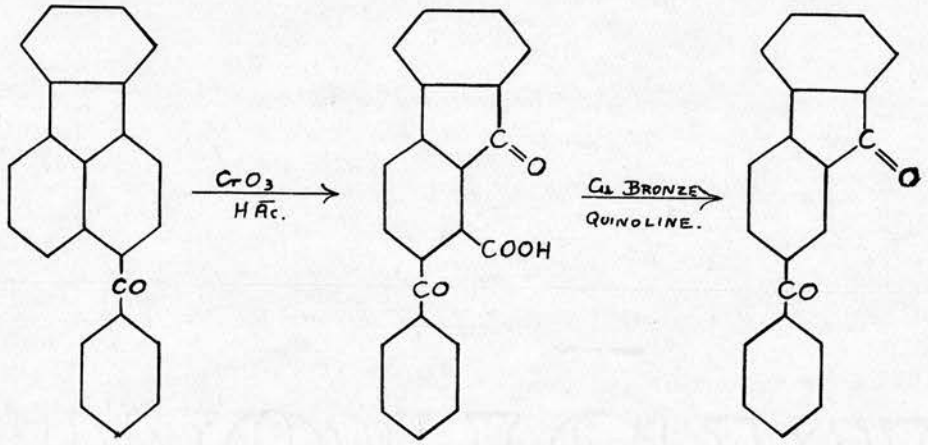
Decarboxylation/

Decarboxylation of 2-benzoyl-fluorenone-1-carboxylic acid.

The acid (0.01 g.) was heated in quinoline with a pinch of copper bronze when a reaction occurred at 180°C. and was complete after 10 minutes at this temperature. The mixture was decomposed with dilute hydrochloric acid and the 2-benzoyl-fluorenone extracted with benzene. The benzene solution was washed free from acid, dried over anhydrous calcium chloride and chromatographed on a column of alumina (4" long x 0.4" diameter). The substance was adsorbed as a yellow band which moved down the column and was ultimately eluted when the column was developed with benzene. The yellow coloured eluate was worked up in the usual way and gave a yellow solid which crystallised from alcohol to give bright yellow needles, M.P. 174.5-176°C. A mixed M.P. with a sample of 2-benzoyl-fluorenone prepared by oxidising 2-benzoyl-fluorene (p.153) gave no depression.

Equation/

Equation for reactions.



2-BENZOYL-FLUORENONE-1-CARBOXYLIC ACID.

2-BENZOYL-FLUORENONE.

Oxidation of 2-benzoyl-fluorene to 2-benzoyl-fluorenone.

cf. Huntress and Hershberg, J.A.C.S., 1931, 53, 2720.

A solution of sodium dichromate (0.185 g.) in glacial acetic acid (1 c.c.) and water (0.25 c.c.) was added to a gently boiling solution of 2-benzoyl-fluorene (0.10 g.) in glacial acetic acid (2 c.c.) and the whole refluxed for two and a half hours. The mixture was diluted into water (20 c.c.) and the 2-benzoyl-fluorenone extracted with benzene. The benzene extract was washed, dried over anhydrous calcium chloride and the solvent evaporated off. This gave a crude yellow solid (0.07 g.), M.P. 164-169°C.

The crude solid was purified by chromatographing

on/

on a column of alumina (4" long x 0.4" diameter) with benzene as solvent. The solid was adsorbed as a yellow band, 2" long, with a little blue fluorescent material emerging from the bottom. Development with a 3:1 mixture of benzene and light petroleum (80-100°) gave a deep yellow eluate which deposited a yellow solid. This was crystallised from alcohol and gave yellow needles, M.P. 175-176.5°C.

Yield (of crude material) = 66.6% Th.

Oxidation of 11-(?) benzoyl-fluoranthene.

A solution of chromic anhydride (A.R., 2.1 g.) in water (1.5 c.c.) and glacial acetic acid (1.5 c.c.) was added slowly to a solution of 11-(?) benzoyl-fluoranthene (0.90 g.) in glacial acetic acid (15 c.c.). The mixture was allowed to stand overnight, raised to the boiling-point and refluxed for 2 hours. The mixture was worked up exactly as detailed for the oxidation of fluoranthene (see p. 150) and gave an orange solid, M.P. 206-209°C. A mixed M.P. with 2-benzoyl-fluorenone-1-carboxylic acid gave a definite depression (184-195°C.). This substance was analysed for 6-(7)-benzoyl-fluorenone-1-carboxylic acid as follows:-

$C_{21}H_{12}O_4$ requires C, 76.83%; H, 3.66%.
found C, 76.83%; H, 3.81%.

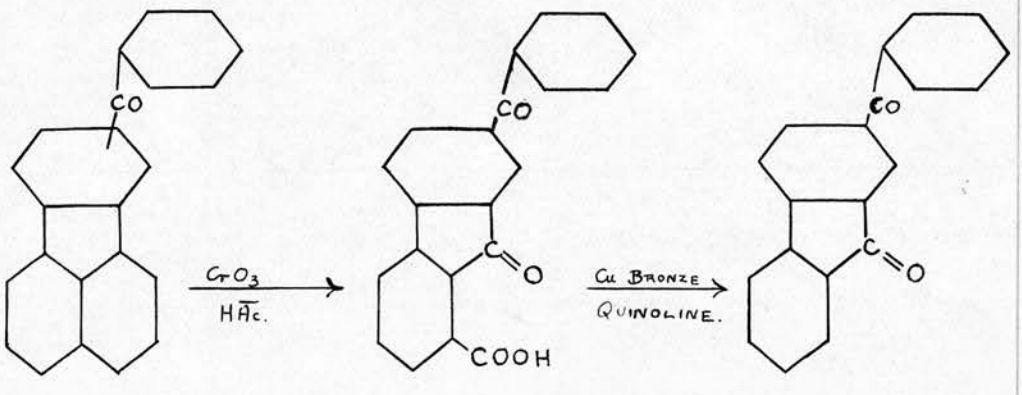
Yield = 0.28 g. = 29% Th.

Decarboxylation/

Decarboxylation of 6-(7)-benzoyl-fluorenone-1-carboxylic acid.

The acid (0.05 g.) was heated in quinoline with a trace of copper bronze when a reaction occurred at 180-185°C. and was complete in 20 minutes. The mixture was decomposed with dilute hydrochloric acid (20 c.c.) and the benzoyl-fluorenone extracted with benzene. The benzene solution was washed free from acid, dried over anhydrous calcium chloride and chromatographed on a column of alumina (4" long x 0.65" diameter). The substance was adsorbed as a uniform yellow band which was eluted with a mixture of 1% alcohol in benzene. This gave a yellow solid (0.04 g.), which was crystallised from alcohol and gave clusters of slightly orange coloured needles, M.P. 174-176°C. A mixed M.P. with 2-benzoyl-fluorenone gave no depression.

Equation for the reactions:-



11-(12)-Benzoyl-fluoranthene.

7-Benzoyl-fluorenone-1-carboxylic acid.

2-Benzoyl-fluorenone.

Oxidation of dibromo-fluoranthene.

A solution of chromic anhydride (A.R., 0.64 g.) in water (6 c.c.) and glacial acetic acid (4 c.c.) was added slowly to a solution of dibromofluoranthene (0.34 g.) in glacial acetic acid (25 c.c.). The dibromofluoranthene was not very soluble in glacial acetic acid.

The mixture was allowed to stand overnight and refluxed for two hours. After this time the dibromofluoranthene had not completely dissolved so more glacial acetic acid (40 c.c.) and chromic anhydride (A.R., 0.70 g.) was added and the mixture refluxed for three hours longer when all the solid was in solution. Half of the acetic acid was distilled off and the remaining solution diluted into water (150 c.c.). The bromofluorenone-1-carboxylic acid was worked up exactly as detailed for the oxidation of fluoranthene (see p. 150). A capillary M.P. was very indefinite and showed charring above 200°C. A micro M.P. showed sintering from 150°C. with slow melting and gradual decomposition from 206-240°C. The substance looked crystalline and pure under the microscope and was analysed for bromofluorenone-1-carboxylic acid as follows:-

$C_{14}H_6O_3Br_2$ requires Br, 41.88%.

$C_{14}H_7O_3Br$ requires Br, 26.40%.

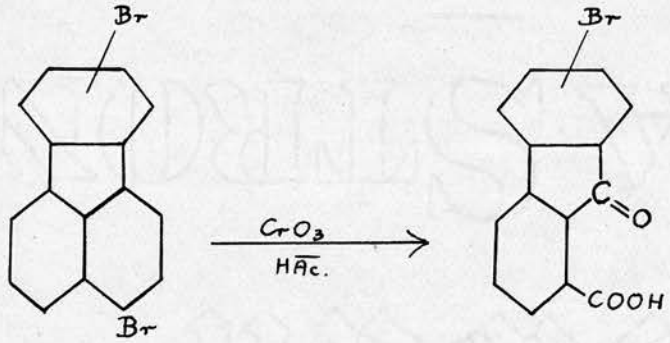
found Br, 27.52%.

This/

This showed that a monobromofluorenone-1-carboxylic acid was obtained as the oxidation product of dibromofluoranthene.

Yield = 0.09 g. = 31.5% Th.

Equation for reaction.



Attempted decarboxylation of bromofluorenone-1-carboxylic acid.

The acid (0.03 g.) was heated in quinoline with a pinch of copper bronze. A brisk reaction occurred at 180-190°C. and was complete after ten minutes at this temperature. The quinoline solution looked very 'muddy' at the end of the reaction. The mixture was decomposed into dilute hydrochloric acid (15 c.c.) and the bromofluorenone extracted with benzene, washed and dried in the usual way. This gave an orange oily solid, M.P. 96-120°C. which was purified by chromatographing/

graphing on a column of alumina (4.5" long x 0.4" diameter) with benzene as solvent. Development with benzene gave a yellow eluate which deposited a yellow solid after concentration. The solid looked cleaner than the original crude material, but still slightly oily, and was crystallised from alcohol (very soluble). An impure colourless solid was deposited, M.P. $< 90°C.$ over a large range. The alcoholic mother liquor was allowed to evaporate slowly and gave yellow crystals, M.P. 90-120°C. Nothing further was done with this substance. Some dark brown material was left at the top of the column but was not investigated.

Further attempt to decarboxylate bromofluorenone-1-carboxylic acid.

The acid (0.03 g.) was heated in quinoline with copper bronze. Slightly less copper bronze was used than in the first attempt. A slight reaction was seen to occur at 160°C. and the temperature was kept at 160-165°C. for half an hour. The quinoline solution looked cleaner than in the first attempt. The mixture was decomposed into dilute hydrochloric acid (15 c.c.) and the bromofluorenone extracted with benzene. Unchanged acid was extracted from the benzene solution with dilute sodium hydroxide solution. The benzene solution was washed free from alkali and dried over anhydrous calcium chloride. Concentration of the benzene/

benzene solution gave a deep yellow oily solid of indefinite M.P. This was purified by chromatographing on a column of alumina (5" long x 0.4" diameter) with benzene as solvent. Development with benzene gave a yellow eluate and left some brown residue at the top of the column. The eluate deposited a yellow solid on concentration but this was not pure and was crystallised from alcohol in which it was very soluble. An impure colourless solid was deposited in small quantity which was similar in appearance and M.P. to that obtained in the first decarboxylation. The alcoholic mother liquor was allowed to evaporate slowly and gave yellow crystals, M.P. 90-154°C. Nothing more could be done to purify this substance because of the very small amount of material available.

TABLE AND COMPARISON OF MELTING-POINTS.

Substance	Page	M.P. (°C.)	Quoted M.P. (°C.)	Reference
4-Bromofluoranthene	59	108-110	103 110	11 48
4-Cyanofluoranthene	62	117-121	112	11
4-Benzoyl-fluoranthene	38	129-130	—	—
2:4-Dinitrophenylhydrazone of 4-benzoyl-fluoranthene	50	260-265	—	—
Picrate of 4-benzoyl-fluoranthene	51	158-160	—	—
Oxime of 4-benzoyl-fluoranthene	51	219-223	c.170	13
Beckmann rearrangement product on oxime of 4-benzoyl-fluoranthene	51	260-263	—	—
11-Benzoyl-fluoranthene	39	120-121	111-112	13
2:4-Dinitrophenylhydrazone of 11-benzoyl-fluoranthene	52	281-284	—	—
Picrate of 11-benzoyl-fluoranthene	52	128-130	—	—
Oxime of 11-benzoyl-fluoranthene	52	193-198	212-213	13
Beckmann rearrangement product on oxime of 11-benzoyl-fluoranthene	53	209-214	c.150	13
Dibenzoyl-fluoranthene	145	173-178	—	—
4-o-Carboxybenzoyl-fluoranthene	77	231-232	230	13
Methyl ester of 4-o-carboxybenzoyl-fluoranthene	71	103.5-105	—	—
Oxime of 4-o-carboxybenzoyl-fluoranthene	79	221-225	207-209	13

11-/

Substance	Page	M.P. (°C.)	Quoted M.P. (°C.)	Reference
11-o-Carboxybenzoyl-fluoranthene	79	227-228	212	13
Methyl ester of 11-o-carboxybenzoyl-fluoranthene	71	172-173.5	180-181	13
Oxime of 11-o-carboxy-benzoyl-fluoranthene	81	232-235	224-225	13
Fluoranthene-4-carboxylic acid	93	283-285	264-275	11
Fluoranthene-11-carboxylic acid	90	278-280	283-285	13
Methyl ester of fluoranthene-11-carboxylic acid	85	93-95	—	—
Fluoranthene-4:11-dicarboxylic acid	91	>350	—	—
Methyl ester of fluoranthene-4:11-dicarboxylic acid	88	183-184.5	—	—
4-Acetyl-fluoranthene	127	131-132	—	—
2:4-Dinitrophenylhydrazone of 4-acetyl-fluoranthene	127	261-262	—	—
Oxime of 4-acetyl-fluoranthene	128	195.5-198	—	—
Beckmann rearrangement product on oxime of 4-acetyl-fluoranthene	128	182-189	241-242	11
11-Acetyl-fluoranthene	117	101-102	68	14
2:4-Dinitrophenylhydrazone of 11-acetyl-fluoranthene	129	299-301	—	—
Oxime of 11-acetyl-fluoranthene	129	173-178	166	14
Beckmann rearrangement product on oxime of 11-acetyl-fluoranthene	129	117-122	191 190	13 14

Diacetyl/

Substance	Page	M.P. (°C.)	Quoted M.P. (°C.)	Reference
Diacetyl-fluoranthene	122	140-142	—	—
1:2:3:4-Tetrahydro-fluoranthene	54	77-78	69 74-75	6 10
4-Bromo-5:6:7:8-tetra-hydrofluoranthene	55	131-133	135	13
4-Benzoyl-5:6:7:8-tetrahydrofluoranthene	132	142-143	—	—
2:4-Dinitrophenylhydra-zone of 4-benzoyl-5:6:7:8-tetrahydrofluoranthene	147	216-217	—	—
x-Benzoyl-5:6:7:8-tetrahydrofluoranthene	138	118-122	—	—
2:4-Dinitrophenylhydra-zone of x-benzoyl-5:6:7:8-tetrahydrofluoranthene	141	>350	—	—
Fluorenone-1-carboxylic acid	150	196-197	191-193	22
2-Benzoyl-fluorenone-1-carboxylic acid	151	227-228	—	—
2-Benzoyl-fluorenone	154	175-176.5	175-177	M., 1902, 23, 926.
7-Benzoyl-fluorenone-1-carboxylic acid	154	206-209	—	—
x-Bromo-fluorenone-1-carboxylic acid	156	>200 with decomp.	—	—
Fluorenone-8-β-propionic acid	149	130-132	137-138	39
2:4-Dinitrophenyl-hydrazone of α-benzoyl-naphthalene	108	248-249	—	—

2:4/

Substance	Page	M.P. (°C.)	Quoted M.P. (°C.)	Reference
2:4-Dinitrophenylhydrazone of β-benzoylnaphthalene	107	231.5-233	257-258	17
Ethyl trichloracetate	96	B.P.164-166	167.1/754.8 mm.	'Dictionary of Organic Compounds'. Heilbron and Bunbury.
Trichloracetamide	96	139-141	141	Ditto.
Trichloracetonitrile	96	B.P. 84-86	83-84	Ditto.

DISCUSSION.

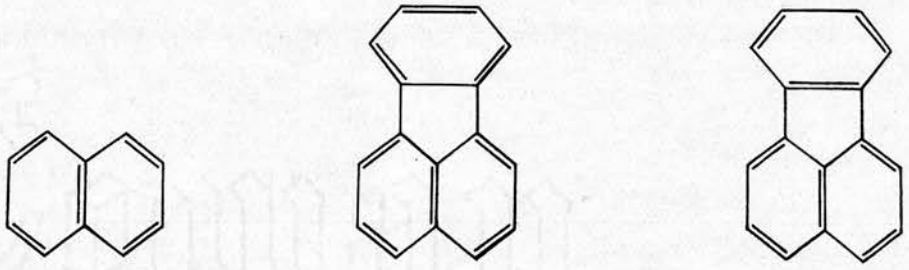
The factor which exerted the greatest influence on the course of the experimental work described in the preceding pages was undoubtedly the use of chromatography. By its application several complex mixtures were successfully separated into their components and on numerous occasions the method was used to purify crude products. Brockmann alumina was invariably used as adsorbent and the standard technique of the liquid chromatogram as described in 'An Introduction to Chromatography' by Trevor I. Williams, p. 35, was used throughout. In some cases the column of alumina was extruded and cut into sections after one or more bands had been eluted. Most separations were simplified considerably by the fact that one or more of the substances fluoresced strongly in ultra-violet light so that a convenient method of following the course of the chromatogram was readily available.

It can be said with confidence that, given the correct conditions of adsorbent and development liquor, it would be ultimately possible to separate any mixture into its components by the use of chromatography. This is not by any means an easy matter, however, and in the present work repeated chromatographing was usually necessary before such an/

an ultimate separation was attained. Considering the many researches in which chromatography has played such a major part, it is unfortunate that relatively little research has been devoted to the study of the subject as a subject. The technique is still largely empirical and there is not yet the certainty about a chromatographic analysis which one experiences when performing a fractional distillation with its thermometer and absolute indication of temperature.

McLeish and Campbell (J.Chem. Soc., 1937, 1103) showed by a study of the reactivity of the bromine atom in variously substituted bromonitronaphthalenes that the double bond distribution in the naphthalene molecule was that shown in I below. Similar methods were applied to the study of hydrindene and tetralin and the results were found to be in agreement with the work of Fieser and Lothrop (J.A.C.S., 1936, 58, 2050). Following on this work and the rule advanced by Fries (Ann., 1935, 516, 248) it can be assumed that the double bond arrangement in the fluoranthene molecule, II below, gives a good representation of the structure which makes the greatest contribution of the six possible contributing forms (neglecting excited/

excited structures) to the resonance hybrid.



I. II. III.

Von Braun, on the other hand, used the formula III in his work without giving any reason for his assignment of the double bonds.

Von Braun showed that bromination, sulphonation and nitration of fluoranthene occur primarily in the 4- position with a relatively small secondary substitution in the 12- position. If one considers the fluoranthene nucleus as being built up of a naphthalene part and a benzene part, then this preferential 4- substitution is not surprising. It has been well established that bromination of naphthalene takes place without a catalyst to give chiefly α-bromonaphthalene. Similarly, low temperature nitration/

nitration and sulphonation of naphthalene give predominantly α-nitronaphthalene and the α-sulphonic acid. These α-compounds would correspond to the 4-substituted compounds obtained in analogous reactions with fluoranthene. In comparison with the easy bromination of naphthalene the bromination of benzene only takes place in presence of a catalyst which would correspond to the more difficult substitution in the 12-position or benzene part of the fluoranthene nucleus.

Von Braun (loc. cit.) claimed that in acylation experiments substitution occurred primarily in the 12-position with a secondary substitution reaction occurring in the 4- position. We have repeated some of von Braun's work in this field and a comparison of the results obtained is given below.

Benzoylation.

Two pure mono-benzoyl-fluoranthenes were separated from the reaction mixture and it was shown fairly conclusively that substitution occurred to an equal extent in both the 4- and 11- positions. Comparative experiments with the normal Friedel-Crafts reaction, as used by von Braun, and the Perrier modification of the Friedel-Crafts reaction gave similar results.

Von Braun proved that bromination occurred in the 4- position by his work on the oxidation of the corresponding/

corresponding amine (see Introduction, pp.13-14) and established a link between his bromo-, nitro- and sulpho- series of derivatives and his acylation series of derivatives (Introduction, pp. 15-17). 4-Benzoyl-fluoranthene was synthesised by us from 4-bromo-fluoranthene and shown to be identical with one of the products of the Friedel-Crafts reaction. We were thus able to establish a further link between the two series of derivatives. The second isomer was shown to be 11-benzoyl fluoranthene (see p. 174).

The oximes, picrates and 2:4-dinitrophenyl-hydrazones were prepared from each of the benzoyl-fluoranthene isomers and the Beckmann rearrangement product prepared from each oxime. The analysis of the picrate of 11-benzoyl-fluoranthene was repeated on the same sample and a nitrogen content of 10.8% obtained which suggested, in spite of the sharp melting-point, the presence of free picric acid in the sample.

Phthaloylation.

Two o-carboxybenzoyl-fluoranthenes were separated as the methyl esters from the reaction mixture in approximately equal amounts. The free acids were obtained by hydrolysis of the esters. These were decarboxylated to the corresponding benzoyl-fluoran-thenes/

thenes and so proved to be the 4- and 11-isomers. The oxime was prepared from each keto-carboxylic acid.

Carboxylic acids.

The acids were prepared in two ways.

(a) A Friedel-Crafts reaction with oxalyl-chloride gave a fluoranthene-monocarboxylic acid and a dicarboxylic acid in an approximate weight ratio of 2:1. The monocarboxylic acid was assumed to be the 11-isomer since it did not correspond to the 4-isomer prepared by acid hydrolysis of 4-cyanofluoranthene. The possible presence of a small amount of the 4-isomer in the mixture was demonstrated but not conclusively. The methyl esters of the 11-isomer and the dicarboxylic acid were prepared.

It was shown that fluoranthene-4-carboxylic acid was easily decarboxylated, whereas the 11-isomer was not. The fact that the dicarboxylic acid was easily decarboxylated to fluoranthene-11-carboxylic acid indicated that the acid was fluoranthene-4:11-dicarboxylic acid.

These results were in agreement with the work of von Braun (see Introduction, p. 15).

(b). Preparation of the acids by the Houben reaction gave essentially fluoranthene-11-carboxylic acid, identified by its methyl ester. The presence of a trace of the 4:11-dicarboxylic acid in the mixture was/

was demonstrated but was not isolated in the pure state. None of the 4- isomer was found to be present.

Buu-Hoï and Cagniant (loc. cit.) acetylated fluoranthene and claimed that 11-acetyl-fluoranthene was obtained exclusively in the reaction without any 4-acetyl- or diacetyl-fluoranthene. These results, they claimed, were in complete agreement with the work of von Braun on the acylation of fluoranthene discussed above.

We repeated their work in detail and showed that, under the conditions of reaction given, 60% of the fluoranthene remained unchanged at the end of the reaction. Two mono-acetyl-fluoranthenes were obtained in approximately equal amounts together with a small amount of a diacetyl-fluoranthene. 4-Acetyl-fluoranthene was synthesised from 4-bromofluoranthene and identified as such in the mixture. By analogy with other reactions already discussed, the second mono-isomer was assumed to be 11-acetyl-fluoranthene and the diacetyl compound 4:11-diacetyl-fluoranthene. The oximes and 2:4-dinitrophenylhydrazones were prepared from each of the mono-acetyl-fluoranthenes and the Beckmann rearrangement product prepared from each oxime.

It will readily be seen, from a comparison of the/

the melting-points of 11-acetyl-fluoranthene (see p.161) as purified by us and as given by Buu-Hoï, that this author obtained only an impure mixture of the two isomers and that, consequently, his statements must be accepted with considerable reserve.

The present work indicates, then, that acetylation, benzoylation and phthaloylation of the fluoranthene nucleus give two series of derivatives concurrently. One series has been shown quite definitely to be the 4- substituted derivatives. The other series is thought to be the 11- substituted derivatives although this has not been proved conclusively. The reaction with oxalyl chloride does not quite fit into this scheme since mainly one isomer, fluoranthene-11-carboxylic acid, was obtained together with a dicarboxylic acid.

It was found that interesting physical relationships existed between the two series of isomers. In the 4- substituted series the compounds crystallised as deep yellow needles, whereas the 11- substituted series crystallised as colourless or almost colourless plates which fluoresced blue under the ultra-violet lamp. The 4- substituted isomers had relatively higher melting-points and were less strongly adsorbed on alumina than the 11- substituted isomers.

Benzoylation/

Benzoylation of 1:2:3:4-tetrahydrofluoranthene gave predominantly one isomer which was proved conclusively, by chloranil dehydrogenation to 4-benzoylfluoranthene, to be 4-benzoyl-5:6:7:8-tetrahydrofluoranthene. The presence in the reaction mixture of a second isomeric benzoyl-tetrahydrofluoranthene and a dibenzoyl-tetrahydrofluoranthene was demonstrated, but these substances could not be isolated in the pure state. The 2:4-dinitrophenylhydrazone was prepared from each of the mono-benzoyl-tetrahydrofluoranthene isomers. It was found that tetrahydrofluoranthene and 4-benzoyl-5:6:7:8-tetrahydrofluoranthene did not form picrates.

This work agreed with the results of von Braun in which he showed that bromination, sulphonylchlorination and phthaloylation of tetrahydrofluoranthene gave exclusively the 4- substituted derivatives.

By analogy with corresponding derivatives of naphthalene and tetralin (tetrahydronaphthalene), it might have been expected that these acylation reactions on tetrahydrofluoranthene would have given 3- substituted derivatives or a mixture of 3- and 4- substituted derivatives. As has been mentioned, naphthalene brominates and nitrates exclusively in the α-position under ordinary conditions, whereas tetralin gives a mixture/

mixture of aryl-α- and aryl-β- substituted derivatives. In Friedel-Crafts reactions, carboxylation, alkylation and acylation give a mixture of α- and β-substituted naphthalenes, whereas tetralin gives β-substituted compounds exclusively (von Braun, Kirschbaum and Schumann, Ber., 1920, 53, 1155; von Braun, Hahn and Seemann, Ber., 1922, 55, 1687).

St. Pfau and Ofner (Helv. Chim. Acta, 1926, 9, 669) found that, in a Friedel-Crafts reaction, acetylation of naphthalene with nitrobenzene as solvent gave 89% of β-acetylnaphthalene and 11% of α-acetylnaphthalene. Benzoylation of naphthalene was done in the same solvent and it was found that the ratio of β-benzoylnaphthalene:α-benzoylnaphthalene obtained was 54:46. Had this reaction given a larger percentage of β-compound, it was intended to carry out a similar experiment on fluoranthene with a view to obtaining 3-benzoyl-fluoranthene. It was considered that the results did not warrant such a trial since a very complex mixture of isomers (possibly 3-, 4- and 11-) could be expected.

The results of experiments in which fluoranthene and tetrahydrofluoranthene were oxidised with chromic anhydride in glacial acetic acid were found to be in agreement with the work of Fieser and Seligman (loc. cit.) /

cit.) and Kruber (loc. cit.).

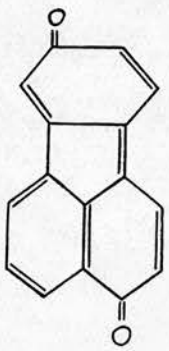
4-Benzoyl-fluoranthene was oxidised with chromic anhydride to a benzoyl-fluorenone-carboxylic acid. This was decarboxylated and the resultant benzoyl-fluorenone found to be identical with a sample of 2-benzoyl-fluorenone prepared by oxidising 2-benzoyl-fluorene. It followed that the acid was 2-benzoyl-fluorenone-1-carboxylic acid. This formed conclusive evidence that benzoylation had occurred in the 4-position in the fluoranthene nucleus.

Following this work, the second benzoyl-fluoranthene isomer was oxidised. This also gave a benzoyl-fluorenone-carboxylic acid which was found to be different from that obtained in the oxidation of 4-benzoyl-fluoranthene but gave 2-benzoyl-fluorenone on decarboxylation. The only possible structure for the acid was therefore 7-benzoyl-fluorenone-1-carboxylic acid. This fixed the substituting position as 11- or 12- in the fluoranthene nucleus and, in agreement with the accepted rules of nomenclature, this series of derivatives has been named throughout by us as 11- derivatives.

In view of von Braun's work on the oxidation products of the quinones, obtained by cyclising the 12-(11-)-o-carboxybenzoyl-fluoranthene, in which he obtained/

obtained two isomeric phthaloyl-fluorenone carboxylic acids (see Introduction, pp. 18-20), we might have expected an isomeric mixture of 6-benzoyl- and 7-benzoyl-fluorenone-1-carboxylic acid from this second oxidation. Only one acid was obtained.

Whilst the two series of mono- derivatives have now been proved to be the 4- and 11- substituted fluoranthenes, there has not yet been any proof regarding the positions of the substituents in a disubstituted fluoranthene. Tobler and co-workers (loc. cit.) claimed that the positions occupied were 4- and 11-. Their argument was that by sulphonation of fluoranthene, a disulphonic acid was obtained which on fusion with alkali gave a dihydroxy compound. This was easily oxidised and gave a typical green quinhydrone body. With the substituents in the 4- and 11- positions such a quinonoid grouping was possible but was not possible with the substituents in the 4- and 12- positions.



They were able to synthesise 4:11-dibromo-5:6-benzofluoranthene from 2:7-dibromofluorene but could not accomplish an analogous synthesis to the dibromo-fluoranthene.

To elucidate this problem of the positions of the substituents in a fluoranthene disubstituted derivative, an attempt was made to oxidise dibromo-fluoranthene. It was expected that either 2:6-di-bromo- or 2:7-dibromo-fluorenone-1-carboxylic acid would be obtained as the oxidation product and that the substance obtained by decarboxylation of this product would be definitely identified as 2:6- or 2:7-dibromo-fluorenone. The results obtained were quite different from those expected and a monobromo-fluorenone-carboxylic acid was obtained as the oxidation product. Further complications occurred in the decarboxylation of this acid and the product was very impure. Because of the small amount available, this end-product could not be purified and identified. The results indicated, however, that bromine was removed from the ring during oxidation and, assuming the starting material to be 4:11- or 4:12-dibromo-fluoranthene, it seemed almost certain that the bromine was being oxidised out of the 4- position or naphthalene part of the molecule.

This/

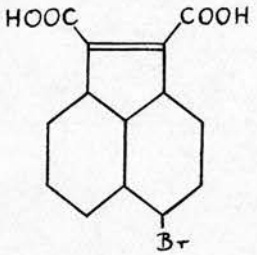
This comparative instability of a bromine-substituted aromatic ring has also been observed with other compounds. For example, Beilstein and Kurbatow (Ann., 1880, 202, 213) obtained phthalic acid by oxidising α-bromonaphthalene with chromic anhydride in glacial acetic acid. No mention of a similar oxidation of β-bromo-naphthalene could be found in the literature. It must be noted, however, that Guareschi (Ann., 1884, 222, 262) obtained a mixture of dibromophthalic acid and dibromo-phthalide when 1:4-dibromonaphthalene was oxidised with chromic anhydride in glacial acetic acid. Oxidation with nitric acid gave a mixture of dibromophthalic acid and bromo-nitrophthalic acid. The same author (Ber., 1886, 19, 135) obtained monobromophthalic acid from a chromic anhydride oxidation of 1:5-dibromonaphthalene.

Although we have assumed that the product from the oxidation of the dibromofluoranthene is a mono-bromo-fluorenone-carboxylic acid, the other possibility of the bromine atom in the 11- or 12- position being lost during oxidation cannot be overlooked. In this case the oxidation product might be a bromo-acenaphthylene dicarboxylic acid I, or the anhydride II. It is probable, however, that these substances will oxidise even further and give 4-bromo-naphthalic acid/

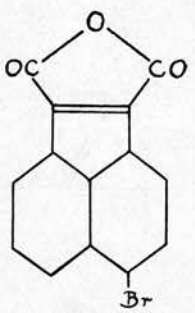
acid III or the anhydride IV. The bromine contents of these substances are given below in comparison with that of a monobromo-fluorenone-carboxylic acid V.

I.	$C_{14}H_7O_4Br$	requires	Br, 25.0%.
II.	$C_{14}H_5O_3Br$	"	Br, 26.55%.
III.	$C_{12}H_7O_4Br$	"	Br, 27.1%.
IV.	$C_{12}H_5O_3Br$	"	Br, 28.9%.
V.	$C_{14}H_7O_3Br$	"	Br, 26.40%.
		found	Br, 27.52%.

The analysis figure thus agrees most nearly with the theoretical for III. The literature gives III as a colourless acid, M.P. 220-221°C. which is easily converted to IV, yellow needles, M.P. 210°C. These observations do not agree with our indefinite melting-point with decomposition, or the fact that our oxidation product was orange in colour.



I.



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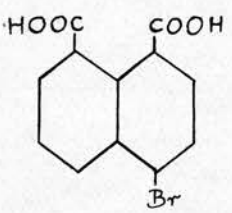
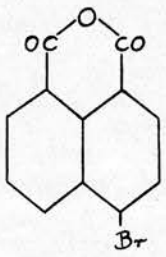
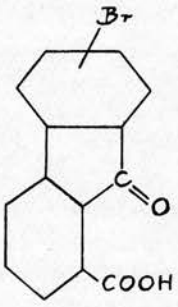


III.



IV.



V.

This work on the oxidation of dibromofluoranthene, especially in the light of the quoted work on the oxidation of bromonaphthalenes, throws some doubt, in our opinion, upon the work of von Braun (loc. cit.) in which he claimed that 4-bromofluoranthene was oxidised to the corresponding 2-bromo-fluorenone-1-carboxylic acid. It may well be, however, that the different temperature used by him (heating on the water-bath) accounts for the rather conflicting results.

These oxidations of the substituted fluoranthenes to the correspondingly substituted fluorenones are potentially fruitful and a further investigation on these lines with a view to clarifying the positions of substitution in a disubstituted derivative would be enlightening.

SUMMARY OF DISCUSSION.

1. It has been shown that in Friedel-Crafts reactions acetylation, benzoylation and phthaloylation of fluoranthene give the 4- and 11- substituted isomers in approximately equal quantities. In some cases a small percentage of disubstituted compound is also formed. This is not in agreement with von Braun's work which claimed that acylation occurred predominantly in the 12-(11-)- position with only small amounts of the 4- substituted isomer.

2. 4-Benzoyl-fluoranthene and 4-acetyl-fluoranthene were synthesised from 4-bromo-fluoranthene, by way of the nitrile, with Grignard reactions. 4-o-Carboxybenzoyl-fluoranthene was decarboxylated to 4-benzoyl-fluoranthene.

3. A Friedel-Crafts reaction with oxalyl chloride gave fluoranthene-11-carboxylic acid and fluoranthene-4:11-dicarboxylic acid in a ratio of 2:1. This agrees with von Braun's results. A preparation of the carboxylic acids by the Houben reaction gave predominantly fluoranthene-11-carboxylic acid.

4. Fluoranthene-4-carboxylic acid (prepared by acid hydrolysis of 4-cyanofluoranthene) was easily decarboxylated, whereas fluoranthene-11-carboxylic

acid/

acid was not. Fluoranthene 4:11-dicarboxylic acid was decarboxylated to fluoranthene-11-carboxylic acid.

5. Benzoylation of 1:2:3:4-tetrahydrofluoranthene gave predominantly 4-benzoyl-5:6:7:8-tetrahydrofluoranthene. This agrees with similar substitutions carried out by von Braun.

6. Benzoylation of naphthalene in nitrobenzene as solvent gave a mixture of 54% α-benzoyl- and 46% β-benzoyl-naphthalene.

7. On oxidation with chromic anhydride in glacial acetic acid and decarboxylation of the product, 4-benzoyl-fluoranthene yielded 2-benzoyl-fluorenone. This proved definitely that the benzoyl group was in the 4- position in the original benzoyl-fluoranthene.

8. Oxidation of 11-benzoyl-fluoranthene with chromic anhydride in glacial acetic acid gave an acid which was different from that obtained in 7. Decarboxylation gave 2-benzoyl-fluorenone which proved that the benzoyl group was in the 11- position in the original benzoyl-fluoranthene.

9. Experiments to orientate a dibromofluoranthene were not completed successfully. The oxidation product may have been a monobromo-fluorenone-carboxylic acid.

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POSTSCRIPT.

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